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## **SiOCN Functionalized Carbon Nanotube Gas Sensors for Elevated Temperature Applications**

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### **ABSTRACT**

**Silicon Oxycarbonitride (SiOCN)** functionalization is proposed for stable, reproducible, reliable and enhanced gas sensing properties in Carbon Nanotube (CNT) gas sensors. The process is very simple: liquid precursor completely coats the surfaces of the CNTs without requiring any surface modification and a **thin layer** of semiconductor ceramic **SiOCN** is created on the CNTs after heat treatment. This new kind of conductometric gas sensors can detect 10 ppm NH<sub>3</sub> and 2 ppm NO<sub>2</sub> at temperatures up to 350°C. The stability of the functionalized CNT sensor is verified up to 520°C, while the CNT sensor without the **SiOCN** coating lost conductance after 250°C due to structural modification. **SiOCN** functionalization of CNT changes the recovery from irreversible to reversible and the recovery time decreases from 60 minutes at 100°C to 19 minutes at 350°C.

### **Introduction**

CNTs are candidates for gas sensing application due to their high surface area and large number of active surface sites. Their electric properties can be influenced by very small amounts of adsorbed

gas molecules even at room temperature [1]. However, there are still limitations to their commercial usage as gas sensors such as long recovery time, detection of limited gases, and the strong influence of humidity. Attempts have been made to improve their performance, including, sensitivity, reproducibility and more importantly the recovery time, by applying secondary phases and forming a composite structure with polymer coatings or metal oxide nanoparticles on the surface of CNTs [1, 2]. In several cases this bond could be achieved only by the functionalization of the CNT surface e.g. acid treatment [3]. These processes are complex and therefore, limit the application of CNTs to sensor technologies. Another problem with the CNT sensors is the limited operating temperature. Because CNTs are very sensitive to air and easily decomposes at elevated temperatures, it is difficult to broaden their potential for applications in the automotive or processing arenas [2].

In this article we demonstrate a simple way to functionalize the surfaces of the CNTs. A continuous **thin layer** of a SiOCN composition can be produced by using a liquid polymer precursor. These structures are shown to have promising gas-sensing properties and stability at temperatures up to 520°C. Our composite material is composed of a carbon fiber substrate (CF), carbon nanotubes (CNTs) with polymer-derived **SiOCN** coating. Polysilazane, which is liquid organic precursor for silicon carbonitride (SiCN) wets and completely coats the surfaces of the CNTs without requiring any further surface modification [4]. A **thin layer** of **SiOCN** can be created by placing a drop of the precursor on a carbon nanotube structure, which is immediately drawn in by surface tension. This organic coating is converted into the amorphous and semiconducting ceramics by controlling the pyrolysis conditions, forming thin film of **SiOCN** on CNTs.

CNTs functionalized as above have been used to create catalysts for hydrogen generation by coating them with a **thin layer** of transition metals. These catalysts have been shown to produce hydrogen from aqueous solutions of sodium borohydride with an extremely high figure of merit, that is, in terms of rate of hydrogen production per gram of the transition metal [4-5]. In this architecture, **SiOCN** interlayer is a critical instrumental in dispersing the transition metals into a **thin layer**. In this paper, however, we focus only on the ternary structure (CF/CNTs/**SiOCN**) and discuss its gas sensing properties. Gas sensing properties of quaternary systems with transition metal coatings (CF/CNT/**SiOCN**/Catalyst) will be reported later.

## Experimental

### 2.1. Ternary CF/CNT/SiOCN preparation:

Single walled CNT were acquired as “Purified HiPCO® Single-Wall Carbon NanoTubes”, from Unidym CA, U.S.A. The procedure described in [4] was used for dispersing and electrophoretic deposition of the tubes. The as-received tubes were dispersed in a mixture of concentrated nitric and sulphuric acids in a ratio of 1:3. Thirty milligrams of the single wall CNTs (SWCNTs) were added to 4 ml acid mixture. The mixture was refluxed for one hour at 130°C. One ml of this solution was extracted, to which 1 M solution of NaOH was added until the pH reached a slightly basic value. At this point the solution became clear, with a yellowish tinge. The adjustment of the pH towards basic causes the migration of the CNTs towards the positive electrode upon application of a DC field (it has been shown that replacing NaOH with salts causes deposition towards the negative electrode [6]). Electrodeposition was carried out with two, 4 cm<sup>2</sup> carbon fiber electrodes (Toray carbon fiber paper), immersed into the nanotube solution, held 5 mm apart. A DC voltage (10 V) was applied for 5 minutes to achieve deposition of the CNTs, forming CF/CNT. At this point SiOCN deposited on the surface of CNTs by dip-coating into a commercial polymer derived ceramic solution, Ceraset (Polysilazane) from Kion, Germany, diluted with acetone to 10wt%. The CF/CNT/SiOCN then pyrolyzed at 1100°C for three hours under flowing Ar, a procedure similar to that described in [7].

### 2.2. Sensor fabrication and characterization:

For the fabrication of sensors, a platinum interdigitated electrode structure was deposited by sputtering over Al<sub>2</sub>O<sub>3</sub> substrate and the heating element was deposited on the backside of the alumina substrate as shown in **Figure 1-a**. The sensor operating temperature can be controlled by the applied voltage to the heating element and the Pt resistance can also be used as a thermometer. CF/CNT/SiOCN paper was simply ground and diluted in ethanol. The suspension of CF/CNT/SiOCN in ethanol was dropped to cast on the prepared electrodes as shown in **Figure 1-b** and **1-c**.

The gas sensing measurements in this study were carried out using a flow through method in a thermostatic sealed chamber with controlled temperature and humidity. Two target gases (NH<sub>3</sub> and NO<sub>2</sub>) with concentrations ranging between 1 ppm and 10 ppm were tested at operating temperatures between room temperature (25°C) and 350°C under synthetic dry air with a constant gas flow rate of 300 mL/min.

For the oxidizing gas NO<sub>2</sub>, the sensor response is defined as:

$$S = \frac{R_{gas} - R_{air}}{R_{air}} \quad (1)$$

where R<sub>gas</sub> and R<sub>air</sub> refer to the steady state resistance measured in gas and in air, respectively. For reducing gas, NH<sub>3</sub>, the sensor response is defined by:

$$S = \frac{G_{air} - G_{gas}}{G_{gas}} \quad (2)$$

where G<sub>air</sub> and G<sub>gas</sub> are the steady state conductivities measured in air and gas, respectively. The response and recovery time of sensors are also calculated. The response time (τ<sub>RESP</sub>) is defined as the time of the sensor response to reach 90% of its final value. The recovery time (τ<sub>REC</sub>) is defined as the time of the sensor response to recover 70% of its baseline value. Each measurement is repeated at least twice to report the representative results. The electrical measurements for gas sensing are acquired in the same test chamber at heating rate of 5°C/10min (0.5°C/min) until 520°C.

Raman analyses were carried out with a modular micro-Raman confocal system from Horiba equipped with a single monochromator (iHR320MST3) and a Peltier cooled CCD camera. A He:Cd laser at 442 nm was used as excitation source, with interference filters on laser lines and edge filters on the signal. Spectra are collected on with 1800 l/mm grating, and 100X objective. The samples are mounted on a motor-controlled x-y stage.

## Results and Discussion

The coating process is illustrated in **Figure 2**. The CNTs (**Scheme 1A**) were electro-deposited on the Carbon fiber substrate (CF). The Carbon Fiber paper is chosen as the substrate because of its relatively high surface area and high conductivity for electron transfer. CNTs on the CF have sharp curvature, which improved the surface activity of the carbon atoms. Once CNTs are deposited on CF (CF/CNT) it was dip-coated with 10% acetone diluted Cereset to form a uniform thin layer of polymeric structure after pyrolysis, as shown in **Scheme 1B**. It is known that silazanes present a good affinity and compatibility to carbon. The wetting characteristics of the CF and functionalized CNTs prevent further attachment of polysilanes precursor, forming SiOCN ceramics after pyrolysis [8-9]. The sample was cross-linked at 300°C for 1 h to form an infusible polymer on CNTs. Finally, it was pyrolyzed at 1100°C for three hours in a flowing Ar atmosphere to form the CF/CNT/SiOCN structure (**Scheme 1C**). The high temperature stability of the SiOCN prevented CNTs from burning off and oxidation during the pyrolysis. The pyrolysis at 1100°C causes CH<sub>4</sub> and H<sub>2</sub> release from the structure, leading to the transformation of Polymer Derived Ceramic (PDC) from liquid polymeric phase (organic) to amorphous ceramics phase (inorganic). In our previous study, the uniformly polymer derived SiOCN ceramic coating with a thickness about the same order of magnitude as the wall thickness of the carbon nanotubes was verified by TGA, XPS and TEM [4-5].

The thermal stability of the prepared materials was studied by measuring the material conductance as a function of the working temperature. The conductance is extremely sensitive to any modification that could occur in the material as a consequence of the thermal stimulus. The thermal protocol consisted of in a sequence of three heating and cooling cycles, from 50°C to the maximum temperature with a heating rate of 0.5°C/min and back to 50°C with the same cooling rate. The three thermal cycles reach a maximum temperature of 250°C, 400°C and 520°C respectively.

In order to observe the structural changes and thermal stability of the CF/CNT/SiOCN sensors, the measurement was performed to CF/CNT sensors without SiOCN functionalization. Results for the change in conductance of CF/CNT specimens under air flow with rate of 300 sccm/min are shown in **Figure 3**. The 1<sup>st</sup> thermal cycle causes the conductance to decrease from  $6.4 \times 10^{-4}$  S to  $4.5 \times 10^{-4}$  S. It returned to the original conductance after cooling to 50°C, indicating a reversible process (**Figure 3**). This trend is common for metallic SWCNTs [10]. The conductance decreases further while

heating above 250°C. This step was not reversible and the sample becomes non-conducting at 400°C, assumedly the structure of CNT and CF are destroyed or decomposed due to harsh environment with the high temperature. The complete loss in conductivity was detected by a non continuous line in the cooling step just after reaching 400°C in **Figure 3**. Clearly the CF/CNT sample (without the SiOCN overlayer) cannot be used near or above 400°C. The last thermal cycle (up to 520°C) was performed and showed in the figure to be coherent with CF/CNT/SiOCN sample.

The conductance change of CF/CNT/SiOCN as a function of temperature, as shown in **Figure 4-a**, is very different from the CF/CNT behavior. During the 1<sup>st</sup> cycle, (same conditions with CF/CNT) the conductance increases slightly from  $2.2 \times 10^{-4}$  S to  $2.6 \times 10^{-4}$  S (**Figure 4-a**). The response is reversible and returns to its original conductance after cooling. This reversible increase in conductance with temperature change is an indication of semiconductive behavior and the similar trends are reported for semiconductive CNT thin films [11]. The second thermal cycle (from 50°C to 400°C) caused a sudden increase in conductance after 250°C and reached a value more than twice that of the starting conductance at 400°C. During cooling, it followed a similar rate by decreasing the conductance from  $4.7 \times 10^{-4}$  S to  $3.6 \times 10^{-4}$  S. While heating in the 3<sup>rd</sup> cycle, the sample conductance follows what was observed during the second cooling step and continues with the same rate up to 450°C. Above this temperature, the material starts to become less conductive until 520°C. While cooling to 50°C, it follows the first sharp decrease similar to the heating step and becomes linear after reaching 440°C. The conductance decreases by following the same rate with the 1<sup>st</sup> and 2<sup>nd</sup> cycle and ends with a value slightly lower than that of the initial value ( $1.56 \times 10^{-4}$  S).

To the best of our knowledge, there are few papers in the literature that have studied the electrical properties of CNTs as a function of temperature in air [12-13]. These studies show that CNTs are very sensitive to high temperatures, and decompose easily when expose to air and have a reversible response only up to 250°C. After 250°C, the conductance decreases irreversibly due to structural modification [12]. The reversible increase in the conductivity ( $\leq 250^\circ\text{C}$ ) is explained by the semiconductor nature of the sample, whereas the decrease in the conductance can be explained by the transformation from semiconductor to metallic behavior [12]. The reversible trend under dry air and humid air up to 250°C is verified for our CF/CNT/SiOCN sensor. The sudden decrease in conductance after 440°C (2<sup>nd</sup> cycle) is also similar to the reported CNT composites [12]. However, the conductance increase in 2<sup>nd</sup> step is an unusual behavior for CNT composites. This interesting behavior may indicate an irreversible structural change or an unwanted interaction between the

CNTs and the PDC. Therefore, all three thermal cycles (1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>) were repeated on the same sample.

The repetition of the conductance measurement resulted in similar tendencies (**Figure 4-b**). The conductance sharply increased and cooling was reversible in the 4<sup>th</sup> step (50-250°C), the 5<sup>th</sup> step showed the same behavior with 2<sup>nd</sup> thermal cycle; following the heating-cooling rate up to 250°C, a sharp conductance increased up to 400°C, following the same cooling rate. In the 6<sup>th</sup> thermal cycle conductance increased up to 440°C, following a sudden decrease in conductance from 440 to 520°C, cooling followed the same rate after 440°C, which was only slightly different than 3<sup>rd</sup> thermal cycle. The overall conductance improvement between the 4<sup>th</sup> and 5<sup>th</sup> steps was around 35%, whereas the overall decrease in conductance from 4<sup>th</sup> to 6<sup>th</sup> was 20% (taken at RT). Repeating the thermal protocols on the same sample one after another and resulting in very similar results suggested that the overall conductance change as a function of temperature is intrinsic behavior of CF/CNT/SiOCN sensors.

The plot of conductivity ( $\sigma$ ) versus the inverse of the absolute temperature ( $1/T$ ) is an effective way to calculate the Activation energies, which are estimated the Arrhenius equation from the slopes given the inset in **Figure 5**:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (3)$$

where,  $\sigma$  is conductivity,  $E_a$  is activation energy, and  $k$  is Boltzmann constant. The activation energy of CF/CNT/SiOCN is calculated as low as 1 meV for the 1<sup>st</sup> step and other cooling steps (<440°C). This kind of extremely small band gap is reported in literature for semi-metallic CNTs whose diameter is slightly greater than 1 nm [14-15]. This is considered as an indication of the formation of thin layer of SiOCN on CNTs.

The activation energy remains unchanged in every cooling step below 440°C. This can be due to the preservation of semiconducting behavior of the composite structure (CF/CNT/SiOCN). However, the behavior is more complex upon heating. The activation energy in the 2<sup>nd</sup> step is  $E_a=0.18$  eV. This value is in the range of reported values for PDCs [16-17]. In a previous study we have reported a similar sudden increase in conductance with increase in activation energy for SiOC sensors [18].

Therefore, we believe that the trend of the 2<sup>nd</sup> step is dominated by SiOCN coating. Above 440°C, the sample shows sudden reactions to both increase and decrease in temperature. This continuous decrease in the conductance is similar to the trends reported for CNT sensors, which are not stable at temperatures higher than 250°C [10].

Micro-Raman spectroscopy is a powerful method for investigating the evolution of carbon phase. We used the technique to explore the structural differences that may explain the different behavior of the conductivity of CF/CNT and CF/CNT/PDC. The Micro-Raman results are shown in **Figure 6**. The G, D and 2D bands located at 1570 cm<sup>-1</sup>, 1360 cm<sup>-1</sup>, and 2700 cm<sup>-1</sup> respectively are present. The tangential mode G-band is typical of SWNT and the D-band is usually considered as indication of amorphous carbon [19] or from defects associated with defective nano-tubes [20]. The 2D-band represents the second order of the D-mode and its intensity is related to the stacking order of graphene sheets along the c-axis [21]. The G band intensity is assumed to be not dependent on defects, and thus the I<sub>D</sub>/I<sub>G</sub> intensity ratio has been used for the evaluation of the defect density since the earliest Raman studies of graphite. Most of the time I<sub>D</sub>/I<sub>G</sub> reflects the abundance of SWNTs. Peak width on the other hand shows the defect states in the structure [19].

Before conductivity measurements the CF/CNT shows a very intense G band at 1569 cm<sup>-1</sup> with small a D band at 1360 cm<sup>-1</sup> and rather broad 2D band at 2727 cm<sup>-1</sup> in **Figure 6** that is similar to the published data for SWNTs [21]. After the thermal treatment (up to 520°C) the spectrum is quite different: we can observe a contribution of fluorescence signal from alumina substrate (reported in **Figure 6** for reference). This also means that lower amount of material can be found on the surface, indicating that CF/CNT material was not stable during heating, in agreement with results of conductivity measurements shown in **Figure 3**. The G and D peaks increased in width and shifted to slightly lower wavenumbers; a new peak appeared at 1477 cm<sup>-1</sup> between the G and D peaks. It is known that the G and D bands merge into one broad signal in amorphous systems [22]. During the electrical measurement, the sample is exposed to air up to 520°C. Certainly, this caused some structural changes in CNT without the functional SiOCN coating. The 2D peak at 1272 cm<sup>-1</sup> is also less intense after heating. A weak 2D-band is associated with a random distribution of graphene sheets that would occur in the case of amorphization [23].



Comparing the CF/CNT and CF/CNT/SiOCN spectra before the thermal treatment, SiOCN functionalization clearly causes a broadening in the D, G and 2D bands but the shift towards lower wavenumber is negligible (**Figure 6-top and bottom**). The intensity of the D mode is larger for the functionalized material than for the CF/CNTs. We observed that the G/D ratio radically decreased from 12.9 (in pure CF/CNT) to 2.6 as SiOCN is incorporated with the CNT structure (CF/CNT/SiOCN). PDCs are known to give intense D band and less intense G band due to the amorphous and disordered carbon phase in its structure [23].

The spectrum remains unchanged even after exposure to air at 520°C. Other than the slight decrease in the G band, no peak shift or peak broadening was observed before and after thermal treatment (after the 6<sup>th</sup> thermal cycle). These results suggest that that SiOCN functionalization protects the structure from structural changes at high temperatures and no oxidation is detected even after repeating the conductivity measurements at 520°C in air.

Ammonia (NH<sub>3</sub>) is an industrial chemical. It is a precursor of various nitrogen compounds (including fertilizers) and refrigerant gas. Since it is toxic, the acceptable ammonia concentration at the working place is 25 ppm for 8 hours of exposure [24]. Therefore, ammonia sensor is expected to detect values below this threshold.

Measurements for the ammonia sensing of CF/CNT sensors were carried out at temperatures up to 200°C (since the conductivity and Raman show the material to be unstable at 250°C). The dynamic responses to 10 ppm NH<sub>3</sub> are reported in **Figure 7**. The conductance decreased in the presence of reducing NH<sub>3</sub>, which is an indication of a p-type semiconductor behavior for CF/CNT sensor. The sensor shows a weak response at RT, and a moderate response at 50°C and 100°C. The response improves significantly at 150°C and 200°C. However, the recovery is almost irreversible at every temperature (common problem in CNT sensors).

The CF/CNT/SiOCN samples also showed a p-type response upon exposure to 10 ppm NH<sub>3</sub> in dry air (**Figure 8**). The most remarkable observation is the recovery of the sensor at 150°C after the ammonia is turned off. The best response is obtained at 200°C, where the response is 0.016, with a response time is 30 minutes and a recovery time of less than 1 hour. By comparing two systems, CF/CNT and CF/CNT/SiOCN, it can be concluded that SiOCN functionalization significantly

improves gas responses at temperatures above 100°C, with the major difference being faster recovery.

Nitrogen dioxide (NO<sub>2</sub>) is a common air pollutant. Health requirements suggest that individuals should not be exposed to 3 ppm for periods longer than 8 h. Therefore, NO<sub>2</sub> gas sensors must be stable and detect extremely low concentrations of NO<sub>2</sub> with high sensitivity [25]. The responses of CF/CNT and CF/CNT/SiOCN sensors at 2 ppm NO<sub>2</sub> are compared in **Figure 9-a** and **10**. The CF/CNT sensor shows a low response at RT with no recovery. The increase in conductance in an oxidizing environment is consistent with p-type behavior. The response was greater as temperature rises from RT to 100°C, but then declines to a negligible level at 200°C. The response time is 16 min at 100°C and 9 min at 150°C. However, because of the drift, it is difficult to comment on the recovery at 150°C. The drift is visible only at high concentrations ( $\geq 2$  ppm) and not visible at 1 ppm (**Figure 9-b**). At 1 ppm, it took more than 1 hour to reach 70% of recovery at 150°C. The change in the conductance is also quite low, in the range of  $4.5 \times 10^{-4}$  S. The sample did not respond to NO<sub>2</sub> at 200°C.

In contrast to the CF/CNT specimen, the conductance change in CF/CNT/SiOCN with 2 ppm NO<sub>2</sub> applied from RT to 200 °C are systematic and recoverable as shown in **Figure 10**. The magnitude of the response increases as the temperature increases, but the recovery time remains essentially unchanged. The response time decreases from 28 minutes (RT) to 13 minutes (200°C). The recovery time changes from 60 minutes at 100°C to 40 minutes at 200°C. No dynamic response was observed at temperatures below 100°C.

Since the CF/CNT/SiOCN sensors are stable at temperatures above 250°C, the NO<sub>2</sub> response was also measured from 200°C to 350°C and reported in **Figure 11**. The sample has been heat treated repeatedly during the electrical measurement (reported in **Figure 4-c**). Although there is a slight decrease in conductance (comparing **Figure 10** and **Figure 11**), CF/CNT/SiOCN sensors gave reliable gas responses even after exposing thermal treatment at elevated temperatures under air (after the 6<sup>th</sup> thermal cycle). The gas responses ( $R_{\text{gas}}-R_{\text{air}}/R_{\text{air}}$ ) remained the same before and after the thermal treatment (**Figure 12**). The response time is essentially independent of temperature between 200°C to 350°C, although the recovery is faster as the temperature increases. The response and recovery times for CF/CNT/SiOCN are plotted in **Figure 12**. The response time decreases

gradually from 21 min at 50°C to 10 min at 350°C. The improvement of the recovery time is more evident. It decreases from 1 hour at 100°C to 19 minutes at 350°C. The unique features of the CF/CNT/SiOCN sensors, in comparison to the CF/CNT, are their high temperature capability, their ability to recover and a systematic and smooth response.

## Conclusion

In this work, novel SiOCN functionalization is proposed for stable, reproducible, reliable, and enhanced gas sensing properties in CNT gas sensors. SiOCN functionalization is very simple process: liquid precursor completely coats the surfaces of the CNTs without requiring any surface modification. After heat treatment, a thin layer of PDC, which is a semiconductor ceramic, was created on CNTs. CF/CNT/SiOCN was simply ground, diluted in ethanol, and drop casted on the electrodes. The sensor operating temperature was adjusted by an applied voltage through the heating element on the back side of the substrate.

The stability of the CF/CNT/SiOCN sensor was verified up to 520°C, while the CF/CNT sensor without SiOCN coating lost the conductance after 250°C due to structural modification. The gas responses to NH<sub>3</sub> and NO<sub>2</sub> were also investigated in both systems. SiOCN coating clearly improved the high temperature stability and gave stable gas responses up to 350°C. However, even when we measured at in a narrow temperature range (RT-250°C), where both sensors are stable, CF/CNT still did not show any noticeable response to neither of the gasses or any improvement with temperature with the recovery being almost always irreversible. SiOCN functionalization changed the recovery from irreversible to reversible and the recovery time decreased from 60 minutes at 100°C to 19 minutes at 350°C. Moreover, due to self limiting thickness it gives a great advantage to prepare the reproducible and reliable sensors. Finally, it was demonstrated that even after repeated heating and cooling cycles, the CF/CNT/SiOCN sensor gives the same gas responses.

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## FIGURE CAPTIONS

**Figure 1.** (a) Schematic view of the CF/CNT and CF/CNT/SiOCN sensor preparation (b) optical microscope image, taken during micro-Raman spectroscopy analysis (c) image of final sensor

**Figure 2.** Schematic view of the preparation of ternary CF/CNT/SiOCN samples. **Scheme 1A.** the CF/CNT structure. **Scheme 1B.** coating with ceraset at RT by spin coating. **Scheme 1C.** the formation of ceramic layer at 1100°C. Ninithi 1.0 Software and ACD Lab release 12.01 is used for drawing. Not drawn to scale.

**Figure 3.** Conductance change of CF/CNT sensor as a function of temperature under dry air. 1<sup>st</sup> thermal cycle is between 50-250°C(●), 2<sup>nd</sup> thermal cycle is between 50-400°C(Δ) .

**Figure 4-a.** Conductance change of CF/CNT/SiOCN sensor as a function of temperature under dry air, (b) thermal cycles repeated on the same sample. 1<sup>st</sup> and 4<sup>th</sup> thermal cycle is between 50-250°C(●), 2<sup>nd</sup> and 5<sup>th</sup> thermal cycle is between 50-400°C(Δ), 3<sup>rd</sup> and 6<sup>th</sup> thermal cycle is between 50-520°C(□).

**Figure 5.** Arrhenius plots of the CF/CNT/SiOCN sensor. The graph is drawn to calculate the activation energies in **Figure 4-a**.

**Figure 6.** Micro-Raman spectra of (top) CF/CNT and (bottom) CF/CNT/SiOCN before (Δ) and after (○) heat treatment at 520°C

**Figure 7.** Dynamic response of CF/CNT sensor to 10 ppm NH<sub>3</sub> from RT to 200°C

**Figure 8.** Dynamic response of CF/CNT/SiOCN sensor to 10 ppm NH<sub>3</sub> from RT to 200°C

**Figure 9-a.** Dynamic response of CF/CNT sensor to 2 ppm NO<sub>2</sub> from RT to 200°C **(b)** Dynamic response of CF/CNT sensor to 1 ppm NO<sub>2</sub> from RT to 200°C.

**Figure 10.** Dynamic response of CF/CNT/SiOCN sensor to 2 ppm NO<sub>2</sub> from RT to 200°C.

**Figure 11.** Dynamic response of CF/CNT/SiOCN sensor to 2 ppm NO<sub>2</sub> from 200°C to 350°C.

**Figure 12.** Gas responses of CF/CNT/SiOCN sensors to 2 ppm NO<sub>2</sub> as a function of temperatures from RT to 350°C. \* indicates the measurement after heat treatment (520°C). Response and recovery times of the CF/CNT/SiOCN sensor are also plotted.