Large-Scale Integrated Carbon Nanotube Gas Sensors

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1. Introduction

Due to the excellent and well-known properties of nanoscale materials, intensive research has been performed in various areas. The one-dimensional nanoscale structure of a nanowire or a nanotube is attractive for use in effective cold cathodes [1], field emitters [2], and vacuum microelectronics [3, 4]. Recently, silicide nanowire has shown the possibility of nanoscale interconnection with low resistance [5, 6]. Additionally, carbon nanotubes have been applied in various applications such as energy storage devices, sensors [7, 8], and actuators. The electrical conductivity of carbon nanotubes (CNTs) is prominent (10^6 S m^−2), and thus CNT films also possess a low sheet resistance while holding an excellent optical transmittance in the visible spectrum comparable to that of commercial indium-tin-oxide (ITO); a transparent CNT film heater has been realized [9].

The one-dimensional nanoscale structure of CNT has a large surface area to volume ratio, which is an advantage for maximizing the surface response. Moreover, the radii, which are comparable to the Debye length, offer greater potential in sensing performance, compared to bulk, by showing sensitive changes upon exposure to gas molecules.

CNTs have been intensively investigated for use in gas sensing devices due to their unique physical and chemical properties [10–18]. It has been proven that CNTs present the p-type semiconducting property due to their unique chirality. The absorbing gas molecules can significantly change the conductivity of CNTs by withdrawing and donating electrons [7, 10, 19]. Moreover, the high surface-to-volume ratio of CNTs provides an advantage in sub-ppm level gas detection. The theoretical concept of using metal-nanoparticle functionalized CNTs has been reported and it has been shown that metal nanoparticles act as reactive sites to target gas molecules. A significant change in electrical conductivity is driven by absorbing target molecules [15–20].

This paper reviews the previous reports on CNT-based gas sensors. It discusses the deployment method of CNTs for large-scale applications with a working mechanism.

2. Fabrication Methods

2.1. Fabrication of CNTs. Generally, three types of method are used to growth CNTs [14]. The first method is the arc-discharge method, which grows single and multi-walled CNTs in a vacuum system under an inert gas atmospheric condition. In laser ablation, a carbon target ablated by intense laser pulses in a furnace and the formed CNTs are collected on a cold substrate. The chemical vapor deposition method is the most popular technique; it uses a gaseous carbon source resulting in vertical grown CNTs. Moreover, quality CNTs can be produced at a reduced growth temperature under 1000°C, which compares favorably to the temperature above 3000°C of the arc-discharge or the laser ablation processes. Recently, the hydrothermal method has been developed for the formation of crystalline particles or films;
this method provides more opportunity for the modification of the CNT configuration [15]. Hetero-structured CNT entities, such as CNT-ZnO film [21] and Fe3O4 nanoscale crystal-treated CNTs [22], have demonstrated the quality heterojunction between CNTs [15].

2.2. Dielectrophoresis. It is an essential process to assign nanostructures at a designated spot for device applications [5, 6]. Dielectrophoresis (DEP) is a promising approach to align nanostructures at a designated position with high reliability and accessibility. A motion is induced by the polarization effect exerting a force on a dielectric particle under a nonuniform electric field condition. The DEP method was performed to align CNTs by dropping the CNT-containing solution between the electric field applied to metal electrodes.

2.3. Inkjet Printing. Although the benefit of nanomaterials has been clarified in various applications, the assignment of manipulating the nanoscale materials with certainty in practical applications still remained. It is an essential and inevitable process to control the nanomaterials at designated positions. Inkjet printing is the demand-oriented technology by dropping ink droplets when required. The drop-on-demand scheme is realistic and large area available approach of locating functional materials [8]. The inkjet printing method provides the schemes of high sensitive CNT-embedded gas sensor units on a wafer-scale by inkjetting carbon-nanotube-contained solution following the conventional lithographical metal lift-off processes.

3. Results and Discussion

3.1. CNT Mats. In the sensor fabrication, a Ti adhesion layer of 5 nm thick was deposited before a 50 nm thick Pt coating on an SiO2-coated wafer. Firstly, a CNTs dispersed solution was prepared by ultrasonic vibrating from the CNTs grown substrate, and then the CNT solution was dropped between Pt electrodes under an ac electric field of 10 V at 10 kHz. The CNTs-connected electrodes were observed by field emission scanning electron microscopy (FESEM, FEI Sirion), as shown in Figure 1. No post contact treatment has been performed to reinforce the contact formation between CNTs to Pt electrodes.

The electrical measurement from the as-placed CNTs on Pt electrodes gave a resistance of 64.5 kΩ swept by Keithley 2400, as shown in Figure 2. There was no significant contact noisy resistance reported as much as Megohm unit [23], which was supposed to be very small [6].

Figure 3 is the CNT sensor response to 100 ppb NO2 gas. The CNT sensor response \( R \) was defined as the ratio \( R = (R_1 - R_r)/R_1 \), where \( R_1 \) and \( R_r \) represent the initial resistance and the reacted resistance to NO2 gas, respectively. Two different magnitude voltages of 0.5 and 2.0 V were applied and four various processing steps were taken to investigate the CNT sensor performance. The first process (I) was the sensor response to NO2 for 50 min showing different responses by changing the applied voltage. A higher input voltage of 2.0 V enhanced the sensing response compared to that of 0.5 V.
applied case. The second process (II) was to recover the initial resistance by UV illumination for a limited time span of 20 min. The third process (III) was performed to investigate the transient NO2 responses and UV light recovery steps for 10 min time spans. The last step (IV) was performed for fully recovering the initial resistance by longer time duration of 60 min, especially for the 2.0 V case.

The UV-illuminated recovery seems to be very effective; otherwise, it takes more than 15 h. The UV illumination decreases the desorption-energy barrier to facilitate NO2 desorption from the CNTs. As clearly shown in the figure, the larger voltage input provided higher response in the first region (I). More details will be discussed in the later part. In the second step (II), the case of a lower voltage of 0.5 V was fully recovered for 20 min, while the higher voltage of 2.0 V was partially recovered. For the transient responses (III), the NO2 sensing and recovery were repeatedly achieved in a 10 min time span. A long recovery time of 60 min was needed to recover the initial resistance for the 2.0 V input case denoted as region IV. It is remarkable that the applied voltage controls the sensor responses. The gas sensing response was improved by increasing the applied voltage. However, the higher applied voltage case required a longer recovery time of 60 min, resulting from the increased transferring carriers from CNTs to electrodes. This can be explained by changes in the Schottky junction formation between CNTs and Pt electrodes, where the work function is 4.5 and 5.65 eV, respectively. A corresponding schematic of the Schottky formation of Pt and CNT contacts is shown in Figure 4.

There exists a potential barrier for the electron transferring from CNTs to the metal. The band bending or built-in potential ($V_{bi}$) of the Pt and CNT connection is given by

$$V_{bi} = \Phi_m - \Phi_s$$

The initial built-in potential is equal to 1.15 eV from the equation. Under the bias ($V_a$), the carrier transferring from CNTs to Pt is enhanced due to the reduced potential barrier as given by

$$V_p = \Phi_m - \Phi_s - V_a.$$  

The easier electron transferring by the forward bias-induced barrier lowering may enhance the gas reacting response, which also explains the longer recovery time for the higher applied voltage case. By increasing the number of transferring electrons from CNTs to the Pt electrode by increasing the input voltage, more electrons might be captured by NO2 molecules resulting in the need of a longer recovery time.

Figure 5 shows the sensor response at an NO2 concentration of 50 ppb. The bias voltage of 2 V was applied, and the experimental conditions and processes were given similar to the case of 100 ppb NO2. The CNT sensor detected the 50 ppb level of NO2 successfully and repeatedly. Due to the low NO2 concentration, the first gas reaction was performed in 20 min, and then the time was spanned as 10 min. This CNT sensor operating at room temperature and atmospheric pressure showed highly sensitive and reliable performances. It is an advantage in fabrication to reduce the processing steps and cost.

3.2. Pd-Decorated CNTs. In preparation of the CNT containing solution, commercial arc discharge synthesized single-wall CNTs (Iljin nanotech, ASP-100) were dispersed in a dimethylformamide (DMF) solution for hydrophilic condition to debundle and stabilize the CNT dispersion in solution followed by centrifugation for 30 min to remove residuals. The supernatant was decanted after the sonication process. The concentration of the CNT solution was approximately 20 μg mL$^{-1}$. To produce the Pd nanoparticle decoration on CNTs, a palladium(II) chloride (Sigma Aldrich) solution was mixed with the bare CNT solution at a volume ratio of 3 : 10. The CNT-containing solution of 0.2 μL was dropped between the Pt electrodes under an ac electric field of 10 V$_{p-p}$ (peak-to-peak) at 1 kHz.

Figure 6 showed the Pd-decorated CNTs on the Pt metal electrodes. The interdigitated Pt electrodes having 10 fingers with a 2 μm gap were presented in Figure 6(a). The image of a single finger was presented in Figure 6(b). The enlarged images were shown in Figures 6(c) and 6(d). The Pt nanoparticle-decorated CNTs were clearly observed. Thermal treatment was performed by a rapid thermal process (RTP 2000, SNTEK), which stabilized the contact between the CNTs and Pt metal electrodes by lowering the contact resistance. Raman spectroscopy was used to investigate the
Figure 6: SEM images of Pd-CNTs between Pt electrodes assembled by the DEP method. (a) Ten finger Pt electrodes, (b) a single finger, (c) Pd-CNTs aligned Pt electrodes, and (d) an enlarged image of (c) [24].

Figure 7: Raman signals of D and G spectra at 632.8 nm excitation showing the defect ratios from the Pd-CNTs treated at different temperatures [24]. The Raman spectra were observed at 632.8 nm excitation (1.96 eV) on the dropped and dried CNT solution on a silicon substrate. Three different types of samples were thermally treated at 300, 450, and 600 °C for 1 min in an N\textsubscript{2} environment. The as-deposited sample was also investigated.

Figure 7 depicts the G band Raman peaks obtained at 1592 cm\textsuperscript{-1} (G\textsuperscript{+}) and 1572 cm\textsuperscript{-1} (G\textsuperscript{−}). The ratio of G\textsuperscript{−}/G\textsuperscript{+} indicates the portion of metallic CNTs. The high peak value of D to G\textsuperscript{−} suggests a band resonance condition or heavy defect. Each peak of D was normalized by the G\textsuperscript{−} peak as the Pd-deposited CNTs showed 0.267 of the D/G\textsuperscript{−} value. By increasing the temperature, the D/G\textsuperscript{−} signal was remarkably reduced to 0.192 and 0.139 at 300 °C and 450 °C, respectively. It is worth noting that the increased defect ratio of 0.552 at a high annealing temperature of 600 °C implies the oxidation of CNTs or damage on the CNT surface. It was found that there exists an optimum heat treating temperature to cure Pd-decorated CNTs, reducing the defect ratio. According to the Raman investigation, the CNT samples were thermally treated at 450 °C after the DEP process for sensor fabrication, which also significantly reduced the initial sensor resistance of 225 MΩ to 220 Ω.
Figure 8: TEM images of Pd-decorated CNT. (a) and (b) are the as-synthesized case and (c) and (d) are thermally treated case, respectively. EDS analyses of (e) and (f) present the transition of chemical composition by a thermal treatment [24].

TEM images of Pd-CNTs are presented in Figure 8 before and after the thermal annealing. The aggregation of Pd nanoparticles was observed from the as-synthesized Pd-CNT sample as shown in Figures 8(a) and 8(b). Otherwise, the thermally treated Pd-CNTs at 450°C provided the uniformly dispersed Pd nanoparticles ranging from 3 to 5 nm in diameter, as shown in Figures 8(c) and 8(d). The EDS analysis was performed to investigate the compositional changes of the Pd-CNTs by thermal treatment. Figure 8(e) depicts the chemical signals of Pd, carbon (C), molybdenum (Mo), and chloride (Cl) as well. The Mo peak and Cl peak mainly originated from the TEM grid and Pd solution of palladium(II) chloride, respectively. After thermal treating at 450°C, the Cl peak was significantly removed, as shown in Figure 8(f), which contributed to reducing the sensor contact resistance.

The two types of fabricated bare CNTs and Pd-CNT gas sensors were loaded in a chamber for NO₂ gas detection with varying concentration levels of 100 ppb, 500 ppb, and 1 ppm. The response time and recovery time were limited to 5 min and 10 min, respectively. The target gas level was modulated by mixing the filtered clean air with pure NO₂ gas (99.999%) in a calibrator with an accuracy resolution of 0.1%. The measurement was performed in an atmospheric pressure condition without vacuum system assistance [25] or a gate control [26], which is an important feature in realizing the practical sensor application. The clean air was used as a base gas and purged for 5 min, which stabilized the base measurement condition. During the purging process, there was little change in resistance values, showing the balanced electron-hole transportation in the steady state.

The sensor response (SR) was defined as the ratio of resistance change \( \text{SR} = \Delta R / R_{ini} \), where \( \Delta R \) and \( R_{ini} \) represent the resistance change by reacting to NO₂ gas and an initial resistance, respectively. The sensor responses were measured at different operating temperatures of room temperature (RT), 88, 145, and 321°C controlled by a ceramic heater with a digital power controller. The temperature was read by a k-type thermocouple. The gas responses from a Pd-CNT sensor and a bare CNT sensor were presented in Figures 9(a) and 9(b), respectively. During the limited response time of 5 min, the maximum response was found at 88°C from the Pd-CNT. For 100 ppb NO₂ detection, the sensor gave 0.25% response at RT without heating but the enhanced response was achieved at 88°C to be 3.67% and 2.79% from the Pd-CNT sensor and the bare CNT sensor, respectively. By increasing the gas concentration, the responses were proportionally increased. At a fixed heating temperature of 88°C, the Pd-CNT sensor response was found to be 8.54% at 500 ppb and 9.91% at 1 ppm, respectively. The enhanced response is attributed to the increase of gas absorption by the heating operation. To investigate the effect of heating temperature, the sensor response was scanned by varying the operating temperature.

At a fixed concentration of 100 ppb, the Pd-CNT sensor was more sensitive at 88°C, giving 3.67% compared to 3.45%
It clearly indicates that there exists an optimum operating temperature. Above the critical temperature, the thermal conductivity of CNTs is decreased due to phonon scattering [28] and accelerates the desorption of gas molecules from the CNTs by lowering the energy barrier, resulting in a decrease of the response [25, 29]. Otherwise, the bare CNT sensor has a higher optimum operating temperature of 145°C with lower sensor response compared to the performance of the Pd-CNTs. It is considered that the contribution of the Pd nanoparticle decoration on CNTs is quite significant in response to NO₂ gas.

Figure 10 presents the sensing mechanism of the Pd-CNTs sensor. A schematic of the Pd-CNT sensor is illustrated in Figure 10(a). The reaction of Pd decoration spots on CNTs was presented in Figure 10(b). Ideally, each Pd nanoparticle on a CNT forms a Schottky contact localizing the depletion region, which hinders the hole carrier mobility. Moreover,
Figure 10: (a) A schematic of the sensor structure of the Pd-decorated CNTs. (b) The enhanced sensing mechanism of Pd-CNTs forming the depletion region by Pd nanoparticles [24].

Figure 11: Gas sensor units fabrication steps [27].

the supply of electron carriers by reacting to the oxidizing gas of NO₂ causes an increase in electron-hole recombination, causing the lower hole carrier density in a CNT, which raises the effect of localizing depletion regions. This reaction conclusively reduces the hole carrier concentration, which increases the sensor resistance, resulting in enhancing the response of the Pd-CNT sensor. It presents the scheme of a highly sensitive Pd-CNT gas sensor working in an atmospheric pressure condition, which is freed from the assistance of a vacuum system or a gate control, which may
Figure 12: (a) A photograph image of 200 gas sensor units fabricated on a 4 in. wafer. (b) Interdigitated electrode fingers from a unit device. Enlarged SEM images of circle spots from (b) to (c) and from (c) to (d). CNT arrays clearly underlaid the Pt electrode fingers [27].

Figure 13: (a) A packed sensor unit. (b) I-V characteristics of the unit sensors [27].
Figure 14: (a) The initial resistance values of unit sensors ranged from 172.7 to 169.2 Ω. NO₂ concentration was varied from 50 to 500 ppb with scanning temperatures. (b) A chart of sensitivity changes by varying temperatures and gas concentrations. (c) A chart of temperature effects on sensitivity by fixing NO₂ concentration. The sensitivity values were normalized by the peak sensitivity for different concentrations [27].

Figure 15: CNT array density was modulated by inkjet printing times. The resistance values were measured to be (a) 170 Ω, (b) 315 Ω, and (c) 575 Ω, respectively [27].
CNT arrays improved the sensitivity and detected 10 ppb level of NO₂.

3.3. Inkjet Method

3.3.1. Gas Sensor Fabrication Steps. The location of nanomaterial at designated positions is an essential process to fabricate nanoscale-structure-embedded systems. Inkjet method was applied to deposit the CNT arrays on a 4 in. wafer. The gas sensor unit fabrication was prepared by following steps: (i) preparing the CNT-contained solution, (ii) inkjetting the CNT-contained solution on an Si wafer, (iii) metal (Pt) patterning on the deposited CNT arrays, and (iv) slicing and packaging a sensor unit. The steps are illustrated in Figure 11. In preparation of CNT-contained solution, commercial CNTs (Iljin nanotech, ASP-100) were dispersed in DMF (dimethylformamide) dispersant to debundle and stabilize the CNT dispersion in solution and then centrifuged for 30 min to remove residuals. The solution concentration of 20 μg/mL was deposited on a 4 in. Si wafer according to the align references. Metal contacts (Pt) were interdigitally formed on the deposited CNT arrays by conventional metal lift-off processes, which provide the structural benefit of metal-sitting on CNT arrays. Due to the benefit of Schottky barrier modulation by adsorbed gas molecules [33] and ensures the responses to gas molecules come from the active entity of CNT arrays.

3.3.2. Packed Units. Figure 13(a) is an image of the packed unit sensor. Figure 13(b) shows that the electrical measurements of unit devices randomly picked from slicing a wafer. The resistance values are uniformly low (169.3–176 Ω) due to the structural benefit of metal-sitting on CNT arrays. An attractive contact architecture of metal-sitting structure provides physically and electrically solid contacts without the posttreatment, such as focused-ion-beam (FIB) assisted metal deposition, which may cause noisy contact resistances [31].

3.3.3. Responses to NO₂ Gas. Figure 14(a) shows the sensor responses to NO₂ gas. For gas sensing, the sensor was loaded in a chamber and then N₂ purged for 10 min to stabilize a base measurement line. The gas responses were performed at different temperature settings by room temperature (RT), 50, 100, and 150 °C. The sensing measurements were performed for 10 min exposure to gas followed by a 10 min recovery period for three times. It showed that the gas sensor is sensitive to NO₂ gas exposure and revealed the changes of sensitivity by temperature modulation. 50 ppb level of NO₂ were detected at RT, 50, and 100 °C. Interestingly, however, no significant change was found from 150 °C case. The sensitivity ($S = \Delta R/R_i$) was defined as the ratio of resistance changes ($\Delta R$) by reacting to NO₂ versus the initial resistance ($R_i$) and was shown in Figure 14(b). Figure 14(c) shows the sensitivity chart by varying temperature at a fixed gas concentration. It clearly presents the tendency of sensitivity changes by heating temperatures. By increasing temperature, the reaction between gas molecules to CNTs is facilitated. However, beyond a critical temperature, the thermal conductivity of CNT is decreased due to the phonon scattering [31] and accelerates the desorption of gas molecules from the CNT with lowering energy barrier resulting in decreasing of sensitivity [32]. The metal-sitting architecture has an advantage to prevent the modification of Schottky barrier modulation by adsorbed gas molecules [33] and ensures the responses to gas molecules come from the active entity of CNT arrays.

3.3.4. CNT Density Modification. Due to the benefit of inkjet printing method, the density of CNT arrays would be modulated resulting in control of resistances as shown in Figure 15. The sensors having a thinner dense CNT arrays were fabricated, which have resistance of 570–590 Ω. Figure 16 showed that the detection level of sensors was reached to 10 ppb NO₂ with uniform performances at room temperature and atmospheric pressure not at vacuum condition [34, 35]. The sensitivity was obtained to be 5.73% for 100 ppb NO₂, which showed the higher response than that of 0.58% from the sensor having a resistance of 170 Ω at room temperature as presented in Figure 14. The improved detecting performance of thinner density case is attributed to the enhanced active area of CNT array by being effectively exposed to gas molecules with less inactive CNT entities resulting from overlapping one to others. Detecting a target

![Figure 16: The thinner CNT array density response to NO₂ gas, which has resistances of 570–590 Ω. The enhanced active area of CNT arrays improved the sensitivity and detected 10 ppb level of NO₂ [27].](image)
gas at the atmospheric condition is a merit in sensor operation and fabrication as well by simplifying the structures. It implies that the controlling exposing surface area of CNT arrays may enhance the reaction to gas molecules to improve sensitivity without a heating or a vacuum equipment. All the samples responded similarly at each gas concentration, which is a strong proof of the uniform fabrication of sensor by inkjet printing method.

3.3.5. CNT Sensor Kit. Inkjet-printed CNT sensor units were fabricated as a portable sensor kit. A single sensor unit was Au-wired on a printed circuit board (PCB) as shown in Figures 17(a) and 17(b). A sensor module has a universal serial bus (USB) port to show its reading value on the display, as shown in Figure 17(c). The sensor module has a rechargeable Li-ion battery. The wafer-scale fabricated CNT unit cells were tested for uniformity to NO$_2$ gas response. The resistance change according to the NO$_2$ gas concentration was previously programmed according to the NO$_2$ gas concentration. Figure 18 shows the setup of the demonstration test. A CNT gas sensor kit was placed in a test box and then a 400 ppb quantity of NO$_2$ was injected into the
3.3.6. Development Prospects. A two terminal device detects the change of resistance due to exposure to the target gas. This structure has the advantage of easy fabrication. As previously discussed, the sensing performance can be substantially enhanced by modulating the operating voltage, heating condition, and functional decoration in the CNT entities. Having a three-device for a transistor would improve the CNT sensor performance, especially in terms of producing a significant reduction in recovery time [36] by means of a gate signal. The CNT has advantages for use as a high sensitive gas sensor that will be available to implantation in a compact package. However, pristine CNTs have certain limits due to their lack of selectivity and long recovery time [16]. To resolve these problems, functionalized CNTs have been proposed and intensively investigated. These functionalized CNTs can be tuned to the binding energy [37] in order to regulate the dynamic response of CNT sensors, leading to a high potential for use in selective gas detection with a quick response.

4. Conclusions

Two types of CNT sensors were fabricated with bare CNTs and Pd-decorated CNTs. The dielectrophoresis method was applied to align the CNTs between the Pt electrodes. Raman spectroscopy revealed that postheat treatment at 450 °C was effective in reducing the chemical residuals, giving a low defect ratio of D/G in the Pd-CNT composition. It has been proved that the localized depletion region formed by Pd nanoparticles on the CNTs significantly improves the sensor reaction at atmospheric pressure conditions by control of the carrier transportation.

Inkjet printing method was used to demonstrate the reliable mass production of highly sensitive CNT-based gas sensors by producing 200 sensor units on a 4-inch wafer. Inkjet method was adopted to control the deposition of carbon nanotubes at designated positions via the modulation of density of CNT arrays. Direct metal patterning above the CNT arrays provide simple and stable contact formation between metal and CNT arrays. The performances of the sensors were uniform and highly sensitive; they were sufficiently sensitive to detect a 10 ppb level of NO2.

Although CNTs are potential materials for use in high sensitive gas sensor applications, their promise has not yet been fulfilled in terms of commercialization, mainly due to the lack of selectivity and repeatability. Commercial success may be attained in the near future by developing high functioning CNTs and an effectively combined sensing mechanism.

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References


