Tuning Carbon Nanofiber Density for Optimized Sensing of Ethanol

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***Abstract*—In this study, we investigated the effect of vertically aligned carbon nanofiber (VACNF) density on ethanol vapor sensing performance. VACNFs were synthesized on Si substrates using plasma-enhanced chemical vapor deposition (PECVD), where varying the acetylene flow rate resulted in different fiber densities. Morphological characterization confirmed that higher acetylene flow leads to improved alignment and denser CNF networks. Raman spectroscopy revealed reduced defect levels and increased graphitization with increasing density. Gas sensing measurements showed that moderate to high CNF densities significantly enhance sensor conductivity and ethanol sensitivity due to improved charge transport paths and increased active surface area. These results highlight the importance of CNF density optimization in designing high-performance gas sensors.**

***Keywords*—Gas sensor, Fiber Density, Raman Spectroscopy**

I. Introduction

Volatile organic compounds (VOCs) such as ethanol play a central role in numerous industrial and environmental processes. However, their uncontrolled emission poses serious health and safety risks, making their rapid and selective detection essential for air quality monitoring, industrial safety, and medical diagnostics. Among the various VOCs, ethanol is of particular interest due to its widespread use and its implications in both occupational exposure and breath analysis. Gas sensors capable of detecting ethanol vapor with high sensitivity and selectivity are thus in growing demand across sectors ranging from environmental monitoring to biomedical applications [1-3].

Nanostructured materials have emerged as promising candidates for enhancing gas sensing performance, primarily due to their large surface-to-volume ratios, tunable surface properties, and high chemical reactivity. In particular, carbon nanomaterials, including carbon nanotubes (CNTs), graphene, and CNFs, have attracted attention for their electrical conductivity, chemical stability, and compatibility with microfabrication technologies. Among these, vertically aligned CNFs (VACNFs) are especially attractive due to their directional orientation, mechanical robustness, and accessibility of their sidewalls for gas interactions [4-6].

The sensing performance of VACNF-based sensors can be influenced by a variety of structural parameters, such as fiber diameter, alignment, and density. While many studies have explored the functionalization and electronic properties of CNFs to improve sensitivity and selectivity [7-9], fewer investigations have systematically addressed how the density of VACNFs per unit area affects the sensor's ability to detect target gases. Since the density directly influences the number of available adsorption sites and the pathways for charge transport, it is expected to play a key role in modulating sensing response.

In this study, we investigate the effect of VACNF density on ethanol vapor sensing performance. VACNFs were grown on silicon substrates using plasma-enhanced chemical vapor deposition (PECVD), and the fiber density was controlled by adjusting growth parameters. The resulting VACNF-based sensors were tested for their electrical response to varying concentrations of ethanol vapor under controlled conditions. By correlating the sensing response with the morphological features of the VACNF films, particularly their areal density, we provide insights into the physical mechanisms underlying gas adsorption and transduction in such systems. Our findings reveal that VACNF density plays a critical role in determining the sensitivity and response dynamics of ethanol detection, offering a straightforward strategy for optimizing sensor performance through nanostructure engineering.

II. Experimental

A. VACNF growth

VACNFs were synthesized on thermally oxidized silicon substrates coated with a 9 nm nickel catalyst layer. The nanofiber growth was carried out using a PECVD technique, employing an AIXTRON Blackmagic CVD system. The process conditions were adapted from a previously established method [10], with modifications to control the resulting CNF density. The deposition process began by introducing hydrogen gas (H_2) into the chamber at a flow rate of 700 standard cubic centimeters per minute (sccm), maintaining a chamber pressure of approximately 9 mbar. During this stage, the temperature was ramped up to 500 °C under a reducing atmosphere. Once the target temperature was reached, acetylene (C_2H_2) was introduced as the carbon source. To investigate the effect of CNF density on sensor performance, different flow rates of acetylene, ranging from 5 to 25 sccm, were employed. Growth was initiated by igniting a 100 W pulsed-DC plasma and maintained for a duration of 20 minutes. After the deposition was complete, the reactor was allowed to cool down under a nitrogen (N_2) atmosphere to prevent post-growth oxidation and ensure sample stability. The variation in acetylene flow enabled the controlled synthesis of CNFs with different areal densities while keeping other parameters constant.

B. Measurement Setup

To evaluate the gas sensing performance, 1 cm × 1 cm square samples were diced from a 4-inch wafer. 100 nm gold with 10 nm titanium (as adhesion layers) contacts were deposited using electron beam evaporation through a shadow

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mask, forming two parallel strips (1 mm wide) at opposite ends of each sample. The devices were placed in a sealed chamber with controlled humidity and temperature (maintained at 25 °C and 55% RH, monitored using an ACS Discovery E-series system). Electrical connections to the electrodes were made using conductive carbon paste. A DC voltage of 1 V was applied using a Keithley 2600B Source Meter to record the sensor response. Sensor response (SR) was quantified as:

$$SR=(R_g\text{-}R_a/R_a)\ \times 100\% \qquad (1)$$

where R_a and R_g represent the sensor resistance in air and in the presence of ethanol vapor, respectively. Ethanol vapors at varying concentrations were introduced by evaporating a precisely measured volume of liquid ethanol, dispensed using a micro-sampler. The ethanol concentration was calculated based on the mass ratio of ethanol to the total air mass in the chamber. The overall measurement protocol followed established procedures, as described in [3, 11]. Fig. 1 illustrates the schematic of the gas testing setup, featuring a fabricated sensor positioned inside the chamber and external electronic measurement devices connected to the sensor.

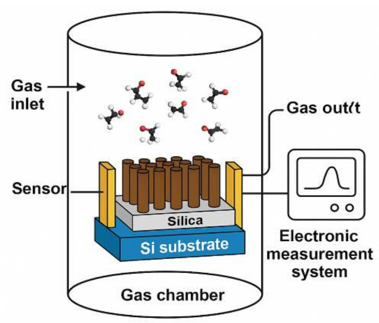

Fig. 1. Schematic of the gas testing setup.

III. Results and Discussion

A. Characterization

The density of VACNFs is a key morphological parameter that significantly affects their surface properties and, consequently, their gas sensing behavior. Among various methods reported in the literature to tune the density of vertically aligned carbon nanostructures, including adjustments in catalyst concentration, growth pressure, temperature, and duration [11-13], we adopted a strategy based on varying the C_2H_2 (acetylene) flow rate during PECVD growth, while keeping the H_2 flow fixed at 700 sccm. This approach effectively modified the H_2/C_2H_2 ratio, which in turn influenced the growth kinetics and fiber density [11].

Fig. 2 displays representative SEM images of CNFs grown at different acetylene flow rates ranging from 10 to 25 sccm. At low flows (e.g., 5 sccm), the fibers appear disordered and entangled, lacking vertical alignment. With increased flow rates, the alignment improves, and the fiber density increases. Top-view SEM images (Fig. 2a–c) illustrate the morphology of three key samples used in gas sensing tests: high-density sample (20 sccm), mid-density sample (15 sccm), and low-density sample (10 sccm). The corresponding fiber densities were estimated to be approximately 8×10^{10}, 6×10^{10}, and 4.5×10^{9} fibers/cm², respectively. These values were derived by statistically averaging counts from multiple SEM images taken at different regions of each sample, with at least three fabrication runs per flow condition to ensure repeatability.

Cross-sectional SEM imaging further confirms the morphological transitions. As shown in Fig. 2d, higher flow rates yield denser and more aligned arrays. Notably, the high-density sample exhibits a highly compact network of nanofibers, whereas the low-density sample shows a sparse distribution with considerable spacing between fibers.

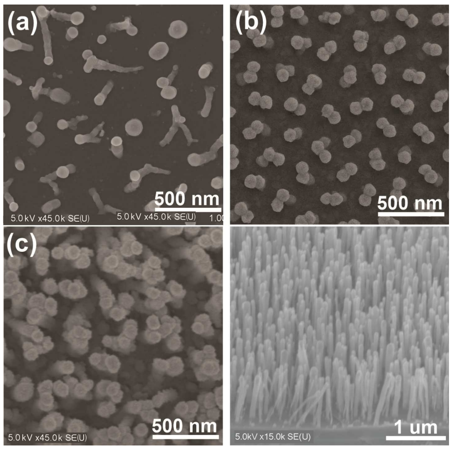

Fig. 2. (a-c) Top and (d) cross-sectional SEM views of VACNFs at different acetylene flows (a) 10 sccm, (b and d) 15 sccm and (c) 20 sccm illustrating density-dependent alignment. (a=low, b=mid, c= high density)

The observed increase in density with acetylene flow is quantitatively summarized in Fig. 3, which plots the fiber number per unit area against C_2H_2 flow rate. The trend suggests that higher acetylene flow enhances CNF nucleation and growth, likely due to an increased supply and decomposition rate of carbon precursors. However, excessive acetylene can lead to a substantial reduction in the H_2/C_2H_2 ratio, thereby diminishing the catalytic promoting effect of hydrogen. This may result in an oversaturation of carbon species, potentially suppressing the formation of stable catalyst clusters required for effective fiber growth [14-16]. These structural differences are crucial because they influence the available surface area, gas diffusion pathways, and charge transport characteristics of the CNFs, all of which are critical parameters in gas sensing performance. The implications of these variations are further explored in the next section.

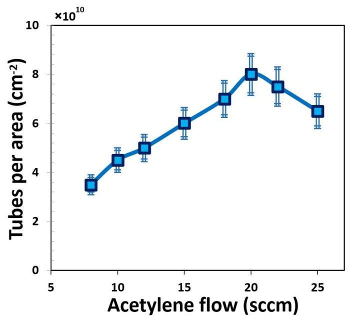

Fig. 3. Number of fibers per area as function of acetylene flow.

Raman spectroscopy was employed to evaluate the structural quality of the CNFs with varying densities. The measurements were carried out using a Renishaw inVia Raman microscope, and the corresponding spectra are presented in Fig. 4. As the density of the nanofibers increases, the number of Raman scattering centers within the probed area also rises, leading to an overall enhancement in signal intensity. Notably, the intensity ratio of the D to G bands, I_D/I_G decreases with increasing fiber density, indicating improved crystallinity and fewer inter-fiber defects in densely packed samples. The G´ band, associated with second-order (2-phonon) scattering processes, becomes more pronounced at higher densities due to the increased number of scattering centers. Additionally, a more distinct D+G band is observed in the high-density samples, which could be attributed to defect formation caused by fiber-fiber collisions or irregular growth at elevated densities [17].

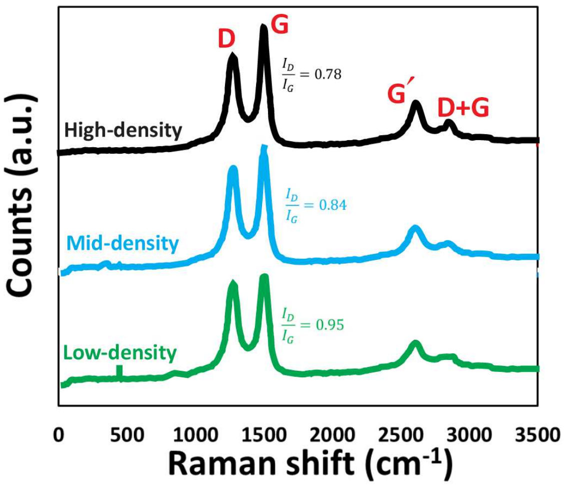

Fig. 4. Raman spectra of different density VACNFs.

B. Gas Sensing Measurements

The gas sensing behavior of the CNF-based sensors with different fiber densities was systematically evaluated through electrical and sensing measurements. The output current–voltage (I–V) characteristics of the sensors are presented in Fig. 5a. All samples exhibited a linear I–V response under both positive and negative bias voltages, indicating the formation of good Ohmic contacts between the metal electrodes and the CNFs. Notably, the conductivity increased with fiber density. This is attributed to the reduced inter-fiber spacing in denser samples, which provides a greater number of conductive paths and minimizes discontinuities in the charge transport network.

To assess their sensing performance, all samples were exposed to varying concentrations of ethanol vapor at room temperature. The corresponding sensor responses are illustrated in Fig. 5b. Upon ethanol exposure, the conductivity of the CNFs changed significantly, reflecting their sensitivity to the analyte. This effect is primarily due to surface interactions between ethanol molecules and the CNFs, which induce charge transfer processes. Specifically, ethanol can donate or withdraw electrons from the CNF surface, modulating the hole concentration in the p-type CNFs and thus altering the resistance of the sensor. The fiber density had a profound influence on the gas sensing performance. In low-density samples, the number of available charge transport paths is limited, leading to a higher likelihood of discontinuities in the conductive network. Consequently, the sensor response may be weak or unstable due to inefficient charge percolation and limited interaction between the gas molecules and the active surface. In contrast, moderate to high-density samples provide multiple parallel conductive pathways, enhancing charge transport and resulting in more stable and pronounced responses to ethanol vapor. Additionally, higher densities increase the accessible surface area for gas adsorption, improving the probability of gas–surface interactions and, thereby, the sensor's sensitivity.

However, our supplementary experiments show when the fiber density becomes excessively high, fiber agglomeration and mutual contact may occur. This reduces the effective surface area available for gas exposure, particularly in the inner regions of the film where gas penetration is limited. As a result, the response can plateau or even decline despite the greater number of fibers. These findings suggest the existence of an optimal CNF density that balances charge transport and surface accessibility, thereby maximizing the sensitivity and response stability of the sensor. This highlights the critical role of morphological control during CNF growth for tailoring gas sensing performance.

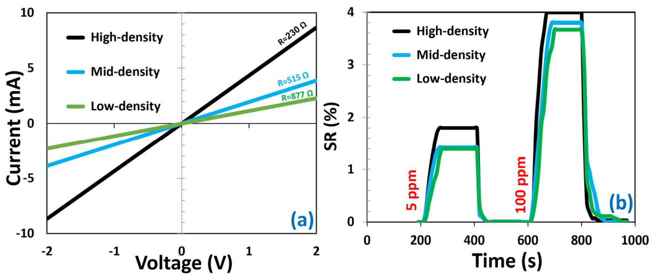

Fig. 5. (a) I–V characteristics of CNF-based sensors with varying fiber densities, showing Ohmic behavior. (b) Ethanol sensing responses at room temperature, highlighting the effect of CNF density on sensitivity.

IV. Conclusions

We demonstrated that the density of vertically aligned CNFs significantly influences their gas sensing behavior toward ethanol vapors. Increasing CNF density enhances conductivity and sensitivity due to better alignment, higher surface area, and more efficient charge transport. However, excessive density may lead to limited gas access in internal regions, suggesting the existence of an optimal density range. These findings provide valuable insight for tailoring CNF-based sensors by controlling nanofiber growth parameters to achieve high sensitivity and reliable performance.

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