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Full Length Article

Long-term stability of superhydrophilic oxygen plasma-modified single-walled carbon nanotube network surfaces and the influence on ammonia gas detection

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ABSTRACT

Single-walled carbon nanotube (SWCNT) networks are subjected to a low-powered oxygen plasma for the surface modification. Changes in the surface chemical composition and the stability of the plasma-treated SWCNT (p-SWCNT) with aging in air for up to five weeks are studied using X-ray photoelectron spectroscopy (XPS) and contact angle analysis. The contact angle decreases from 120° of the untreated hydrophobic SWCNT to 0° for the superhydrophilic p-SWCNT. Similarly, the ratio of oxygen to carbon (O:C) based on the XPS spectra increases from 0.25 to 1.19, indicating an increase in surface energy of the p-SWCNT. The enhanced surface energy is gradually dissipated and the p-SWCNT network loses the superhydrophilic surface property. However, it never revert to the original hydrophobic surface state but to a metastable hydrophilic state. The aging effect on sensitivity of the p-SWCNT network-based ammonia sensor is investigated to show the importance of the aging process for the stabilization of the p-SWCNT. The best sensitivity for monitoring NH_3 gas is observed with the as-prepared p-SWCNT, and the sensitivity decreases as similar as the p-SWCNT loses its hydrophilicity with time goes by. After a large performance degradation during the aging time for about two weeks, the response characteristics including sensitivity and response time of the p-SWCNT to ammonia gas are stabilized and eventually saturated.

1. Introduction

Carbon nanotubes (CNTs), as individual CNTs, CNT networks, or polymer/CNT composites, have recently, because of their unique physiochemical properties, been the focus of intensive research interest as high sensitivity sensing elements for chemical and biological detection. Due to the chemical inertness of CNTs, chemical and biological sensors based on pristine CNTs have certain limitations, such as very low sensitivity to analytes and lack of selectivity, because pristine CNTs have no defect sites or functional groups required for gas adsorption or biomolecule immobilization. Several investigators demonstrated that the sensitivity of CNT-based chemical sensors can be significantly improved by introducing defect sites along the sidewall of the CNTs when exposed to oxygen-based plasma or ultraviolet light (UV/O_3) [1–4]. These results are consistent with theoretical calculations indicating that defect sites on CNTs result in a strong chemisorption of gas molecules and a large charge transfer interaction, while the defect-free CNTs interact weakly with gas molecules and negligible charge transfer [5,6]. However, plasma-treated CNTs were voluntarily reverted to their original surface states over time [7,8], similar to hydrophobic recovery observed in other material systems exposed to oxygen plasma [9–11]. Thus, the stability of plasma-induced changes on the CNT surface and defects over a desired time period is an important issue in view of its practical application potential.

In this study, we examine the chemical and morphological surface modifications of single-walled CNT (SWCNT) networks induced by radio-frequency (RF) oxygen plasma treatment and after aging in air. Additionally, we estimate the influence of aging on the performance of ammonia gas sensors based on plasma-treated SWCNT (p-SWCNT) networks. A controlled number of defect sites along the SWCNT sidewall were intentionally introduced using oxygen plasma. Samples were plasma treated for 10 s at 15 W RF power. The p-SWCNTs have oxygen-containing functional groups,

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which act as anchoring sites for the chemisorption of gas molecules. Oxygenated functional groups created on the surface of the SWCNT were found to dramatically increase sensitivity to target analytes or exhibit exceptionally fast response times. The effect of aging on device stability was investigated over a period of five weeks and characterized by the contact angle. Contact angle and X-ray photoelectron spectroscopy (XPS) measurements were carried out to study hydrophilization change and hydrophobic recovery and to examine the chemical structure of the modified surface.

2. Experimental methods

SWCNTs were purchased from Hanwha Nanotech Co. (Incheon, Korea). To prepare a CNT-dispersed solution for spraying, 3 mg of SWCNTs diluted with 150 mL dichlorobenzene (Sigma–Aldrich, USA) was tip-sonicated for 20 min. After ultracentrifugation of the homogenized solution at 4 °C and 20,000 rpm for 20 min, the SWCNT-dispersed supernatant was separated from the SWCNT aggregates containing many other insoluble materials.

NH_3 gas sensors were fabricated on the glass substrate. Fig. 1a shows a schematic of the NH_3 gas sensing device based on p-SWCNT network which forms gas sensitive active layers between the two interdigitated electrodes as shown in Fig. 1b and c. The electrodes consist of interdigitated palladium lines whose width and spacing are the same as 50 μm. The overall dimension of the glass is 8 mm × 3 mm. To initiate the process, 4-in. glass wafers were sequentially rinsed with acetone, isopropyl alcohol, and deionized (DI) water, followed by drying under nitrogen gas. Next, a SWCNT network film was spray-coated over the entire substrate using the dispersed SWCNT solution and patterned using O_2-plasma etching. The film thickness was controlled by holding the spray conditions constant and varying the amount of deposited material. An atomic force microscopy (AFM) system was used to measure the SWCNT film thickness. Several lateral AFM scans across the steps were taken and their average was calculated to obtain the film thickness (about 35 nm). Pd electrodes (300 Å thick) were deposited on the SWCNT film by lift-off with optical lithography using negative photoresist.

Finally, the SWCNT film surface was treated by RF O_2 plasma. The typical plasma treatment parameters were an O_2 flow rate of 30 sccm, an RF power of 15 W, and a substrate temperature of 25 °C.

XPS was used to analyze the surface of the untreated and treated SWCNT networks. The XPS data were obtained using a SIGMA PROBE Electron Spectroscopy for Chemical Analysis Spectrometer. Survey scans and high-resolution scans of the C1s and O1s peaks were acquired at two spots per sample film. Small peak shifts

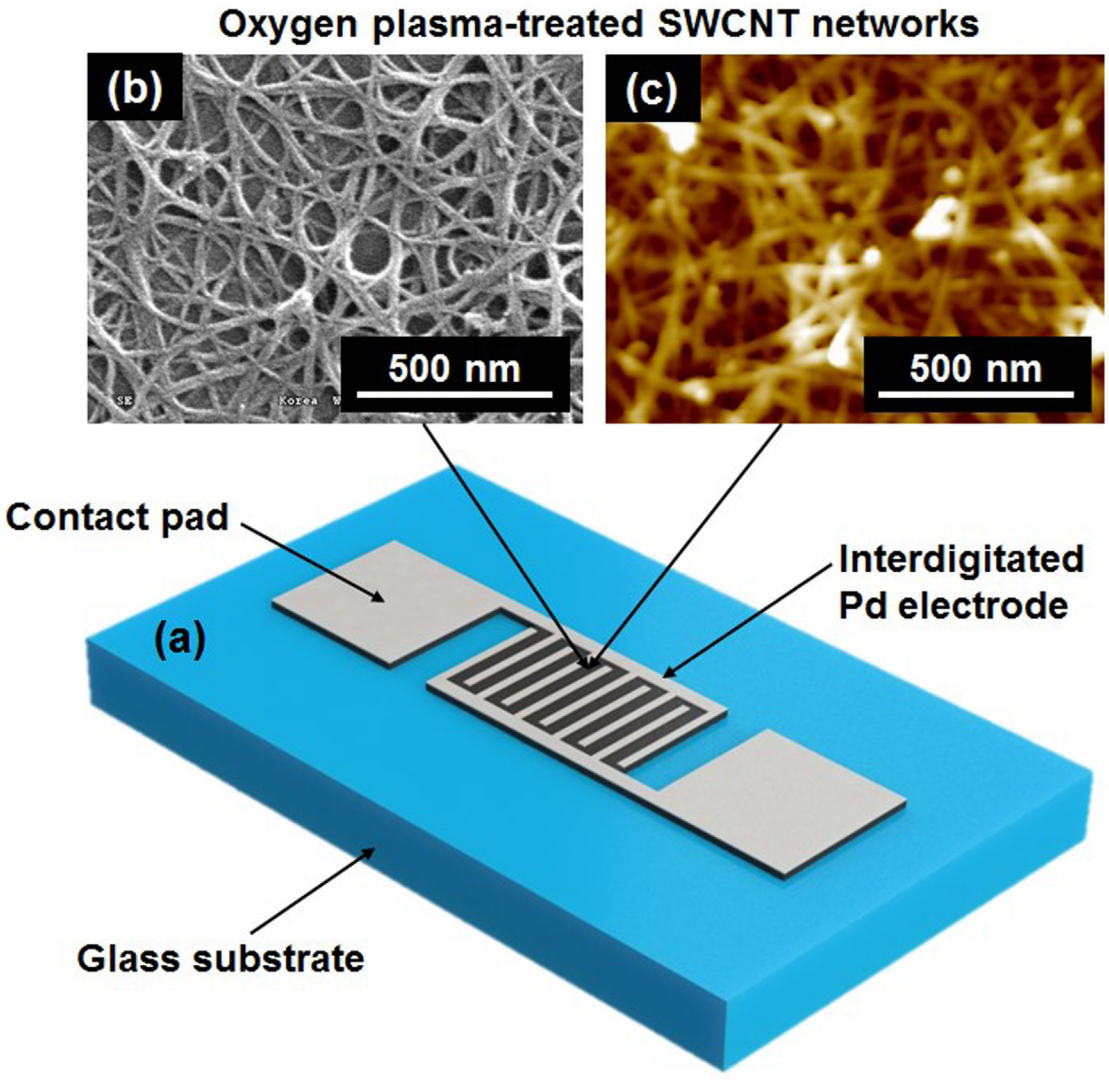

Fig. 1. (a) An oxygen-plasma-treated SWCNT network ammonia gas sensor fabricated on a glass substrate. (b) SEM and (c) AFM images of the oxygen-plasma-treated SWCNT network.