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P-N Junction Effect of Multi-walled Carbon Nanotubes Array on Gas Detection[†]

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Abstract

Abstract (italic typeface) Multi-walled carbon nanotubes (MWCNTs) array of about 40 nm in diameter and 500 to 1300 nm in length was directly grown on Au interdigitated electrodes by radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD). The growth catalyst of Ni_3C*-Ni at the tip of the MWCNTs array was observed by transmission electron microscope (TEM) and selected area electron diffraction (SAED). The sensing properties of MWCNTs arrays to* NO_2*,* H_2S*,* CH_3SH *and* C_8H_{10} *were investigated at operating temperature from 100 to 250 °C. The resistance change to sulfur gases was higher than* NO_2 *and* C_8H_{10}*. It was suggested that Ni at the tip was sulfidized to be* Ni_xS *in sulfur gas and that the p-n junction was formed at the interface between p-type MWCNTs and n-type* Ni_xS*.*

KEY WORDS: (MWCNTs), (Ni_xS), (p-n junction)

1. Introduction

The structural control of carbon nanotubes (CNTs) is very important for electronic applications because their electronic and mechanical properties depend on their structural parameters such as diameter, length, and chirality. The CNTs are also necessary to be grown at low temperature on the substrate such as polycarbonate for industrial application. In recent years, the single-walled carbon nanotubes (SWCNTs) electrodes for sensor devices have been developed by patterning Pt comb-like micro-electrodes with 50 μm gap on the single-walled carbon nanotubes (SWCNTs) grown on the alumina substrate for 1 ppm NO_2 and Cl_2 detection[1)], Pd comb-like electrodes with 80 μm gap on them for 1% H_2 detection[2)], and Au comb-like micro-electrodes with 100 μm gap on them for 50 ppm NO_2 detection[3)]. Multi-walled carbon nanotubes (MWCNTs) have never been directly grown on the Au interdigitated electrodes for gas detection.

In our previous research, MWCNTs were directly grown on anodic porous alumina with Ni catalyst[4)], and carbon nanofibers on the quartz substrate with Au-Pd catalyst[5)] for growth control of MWCNTs using chemical vapor deposition (CVD). A high temperature of 700 °C is necessary for CVD growth of MWCNTs. Under a reducing atmosphere of ethanol or acetylene, the interface between Au interdigitated electrodes and quartz substrate is chemically etched and peeled off. In order to prevent the chemical etch of the electrodes, the growth of MWCNTs should be conducted at low temperature.

In this paper, the MWCNTs array was directly grown on the Au interdigitated electrodes with 5 μm gap and 50 teeth at a low temperature of 350 °C by radio frequency plasma-enhanced chemical vapor deposition (RF-PECVD). The sensing properties of the Au interdigitated electrodes with MWCNTs arrays were examined with various gases: NO_2 as a pollutant gas, C_8H_{10} as a volatile organic compound, H_2S and CH_3SH as bad smelling gases.

2. Experimental

2.1 Fabrication of sensor device

Thin films of Ti / Ni were deposited via the mask limited to 1mm square area by vacuum evaporation on the growth substrate as shown in **Fig. 1**. The Au interdigitated electrodes had been fabricated by a usual ultraviolet photolithography technique. The role of Ni is as the growth catalyst of MWCNTs in the RF-PECVD process. The Ti film acts as a buffer layer to prevent the formation of nickel silicide, which is unfavorable for the growth of the MWCNTs.

2.2 Growth of multi-walled carbon nanotubes array

The growth substrate was set as a cathode in a

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vacuum chamber, as shown in **Fig. 2**. H_2 was introduced into the chamber at 250 Pa after evacuation at 5.0 × 10^{-3} Pa. In hydrogen plasma treatment, the nickel thin film was treated for 20 min at 350 °C by H_2 plasma of 500 W to be nano convex surface. Continuously, the gas mixture of CH_4 and Ar (1/1 in volume ratio) was introduced into the chamber. The carbon species excited for 10 min at 350 °C by CH_4 plasma were vertically diffused and dissolved into the convex surface of the Ni film, leading to the vertical growth of MWCNTs array as show in **Fig. 3**.

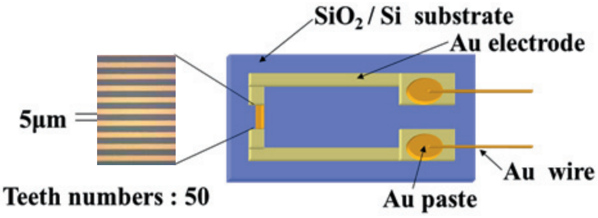

Fig. 1 The schematic diagram of sensor device.

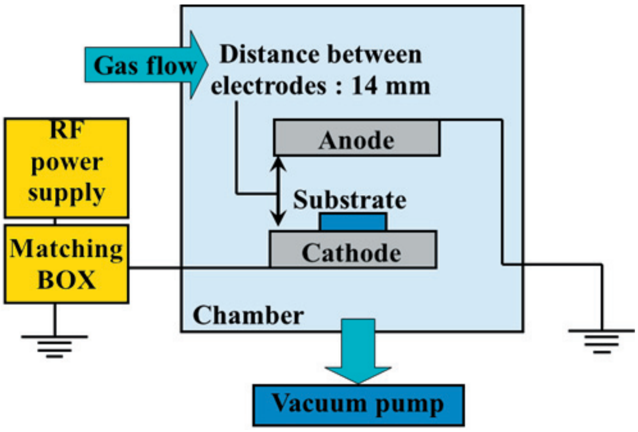

Fig. 2 The schematic view of RF-PECVD apparatus.

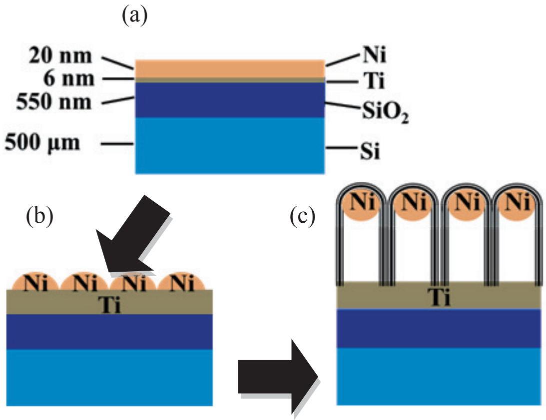

Fig. 3 MWCNTs array growth process: (a) vacuum deposition, (b) H_2 treatment and (c) CNTs growth.

2.3 Characterization

The structural features of the MWCNTs array synthesized were examined by field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and selected area electron diffraction (SAED)

2.4 Gas sensing properties

The sensing properties of MWCNTs array to 1 ppm NO_2, H_2S, CH_3SH and C_8H_{10} were investigated at operating temperature from 100 to 250 °C. The exposure time to Air is 0 to 3 and 8 to 13 min, that to Air-containing 1 ppm various gas 3 to 8 min. The resistance change to NO_2 as a oxidant gas can be obtained as [Ra - Rg] / Ra × 100, where Ra is the resistance in air and Rg that in air-containing 1 ppm NO_2. On the contrary, the resistance change to H_2S, CH_3SH and C_8H_{10} as a reductant gas is expressed by [Rg - Ra] / Rg × 100.

3. Results and discussion

The MWCNTs array was directly grown on the Au interdigitated electrodes by RF-PECVD at 350 °C. The nano convex surface of Ni film for the growth of MWCNTs was formed by H_2 plasma treatment. The MWCNTs array synthesized had ca. 40 nm diameter and three kinds of length (550, 866 and 1300 nm), as shown in **Fig. 4**.

The TEM image, which MWCNTs have tubular structure and Ni catalyst at the tip, is shown in **Fig. 5**. The Ni catalyst size was about 40 nm in diameter, corresponding to the diameter of MWCNTs. The SAED patterns of black circular area indicated the growth catalyst of MWCNTs remained as C, Ni, and Ni_3C at the tip of MWCNTs. The diffraction of C(002) showed that carbon layers existed in parallel with the fiber axis of MWCNTs. This arc-like diffraction corresponds to the

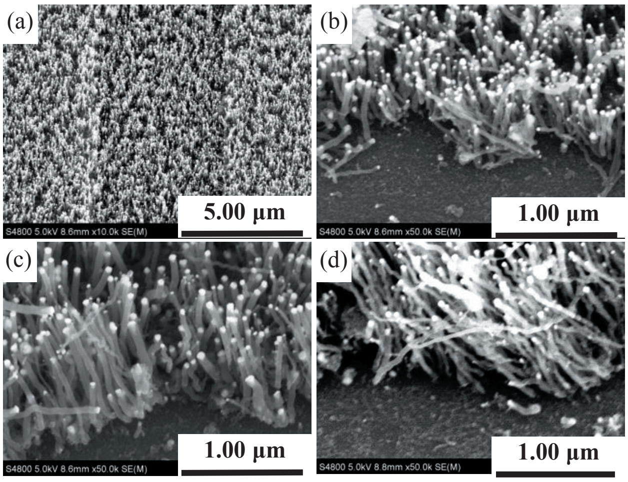

Fig. 4 FE-SEM images of MWCNTs array on the Au interdigitated electrodes: the image of (a) is observed at an angle of 30 degrees, the magnified images of the edges of (b), (c) and (d) correspond to 550, 866 and 1300 nm in length, respectively.

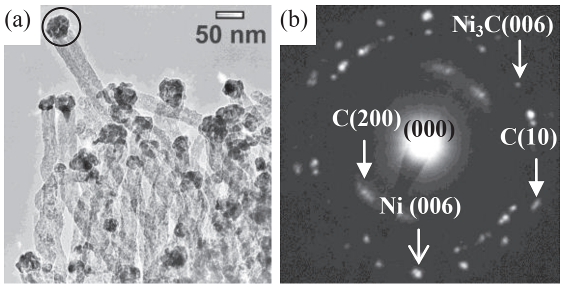

Fig. 5 (a) TEM image of MWCNTs array and (b) the black circular area is the SAED patterns of a MWCNT tip.

tubular structure. The diffraction of Ni(002) and $Ni_3C(006)$ denoted that Ni accelerated the growth of MWCNTs at the tip.

Figure 6 shows the resistance change of MWCNTs array with 866 nm length to 1 ppm NO_2 at 100 to 250 °C. The sensor response at 100 °C showed good response-recovery characteristics. The discrete Ni_3C-Ni droplets at the tip of MWCNTs did not affect NO_2 adsorption at 100 °C. The surface of Ni_3C-Ni could be oxidized to be NiO-Ni_3C-Ni at 150 to 250 °C in air. The resistance of NiO increases with increasing oxygen concentration[6]. At higher temperature, NO_2 is considered to occupy the adsorption sites of oxygen species because the oxidation power of NO_2 is generally higher than that of O_2. On the other hand, the response became slow due to the decrease in hole concentration of NiO at operating temperature more than 150 °C.

Figure 7 shows the resistance change per unit length of MWCNTs array to various gases at 100 to 250 °C. The MWCNTs array with longer length had high specific area, contributing large amounts of gas adsorption sites. However, MWCNTs array with shorter length exhibited higher resistance change to various gases at all operating temperature. In our previous study, when the relative intensity ratio of G-band to D-band, i.e., G/D ratio, was low, the sensor response of MWCNTs to 5 ppm NO_2 was increased, suggesting the contribution of the defect of carbon (D-band) to gas adsorption sites. In this study, it was also clarified that MWCNTs array with shorter length had lower G/D ratio (the related data is not shown here).

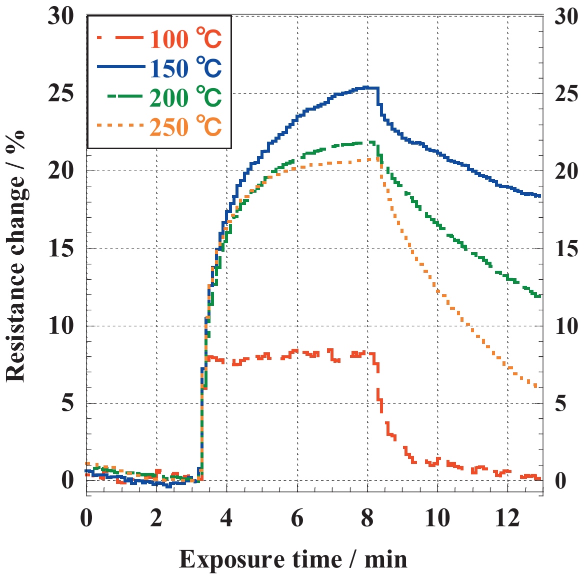

Fig. 6 The resistance change of MWCNTs array with 866 nm in length to 1 ppm NO_2 at operating temperature from 100 to 250 °C.

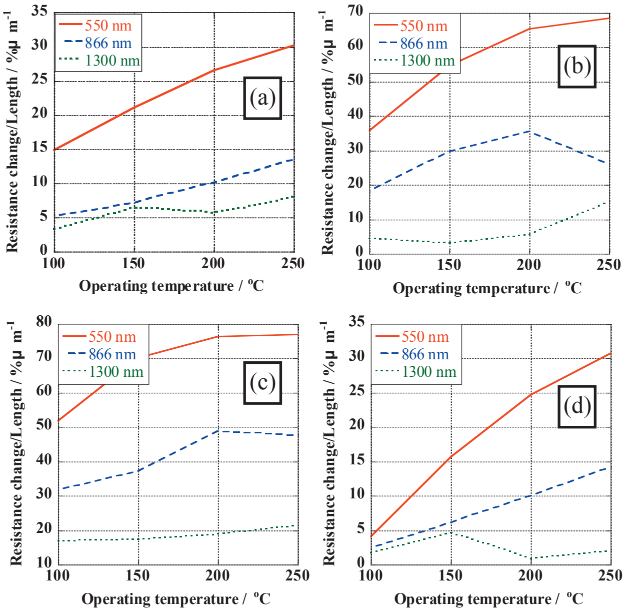

Fig. 7 The resistance change per unit length of MWCNTs array to 1 ppm various gases at 100 to 250 °C: (a) NO_2, (b) H_2S, (c) CH_3SH and (d) C_8H_{10}.

The selectivity of gas detection for MWCNTs array is shown in **Fig. 8**, as the resistance change. MWCNTs array showed excellent selectivity to the sulfur gases of H_2S and CH_3SH. This behavior is related to two factors: (1) increasing the number of gas molecules with decomposition of sulfur gases at high temperature, and (2) the formation of p-n junction at the interface between p-type MWCNTs and the n-type Ni_xS generated by the reaction of NiO-Ni_3C-Ni on the surface of Ni catalyst with sulfur gas. In the case of (1), H_2S reacted with adsorbed oxygen species on the surface and converted into SO_2 and H_2O, as described in ref. [7]. It was reported in the ref. [8] that CH_3SH was converted into CO_2, SO_2, HCHO, CH_3SCH_3 and CH_3SSCH_3. However, CH_3SH was not decomposed at 100 °C [8]. The resistance change to 1 ppm CH_3SH at 100 °C mainly seems to depend on the gas adsorption.

The surface of NiO-Ni_3C-Ni could be sulfidized to be NiS-NiO-Ni_3C-Ni at 150 to 250 °C in sulfur gases. It was evident that Ni_xS had n-type semiconductor properties[9]. Therefore, MWCNTs array showed higher selectivity to H_2S and CH_3SH than NO_2 and C_8H_{10} by forming the p-n junction between p-type MWCNTs and n-type Ni_xS.

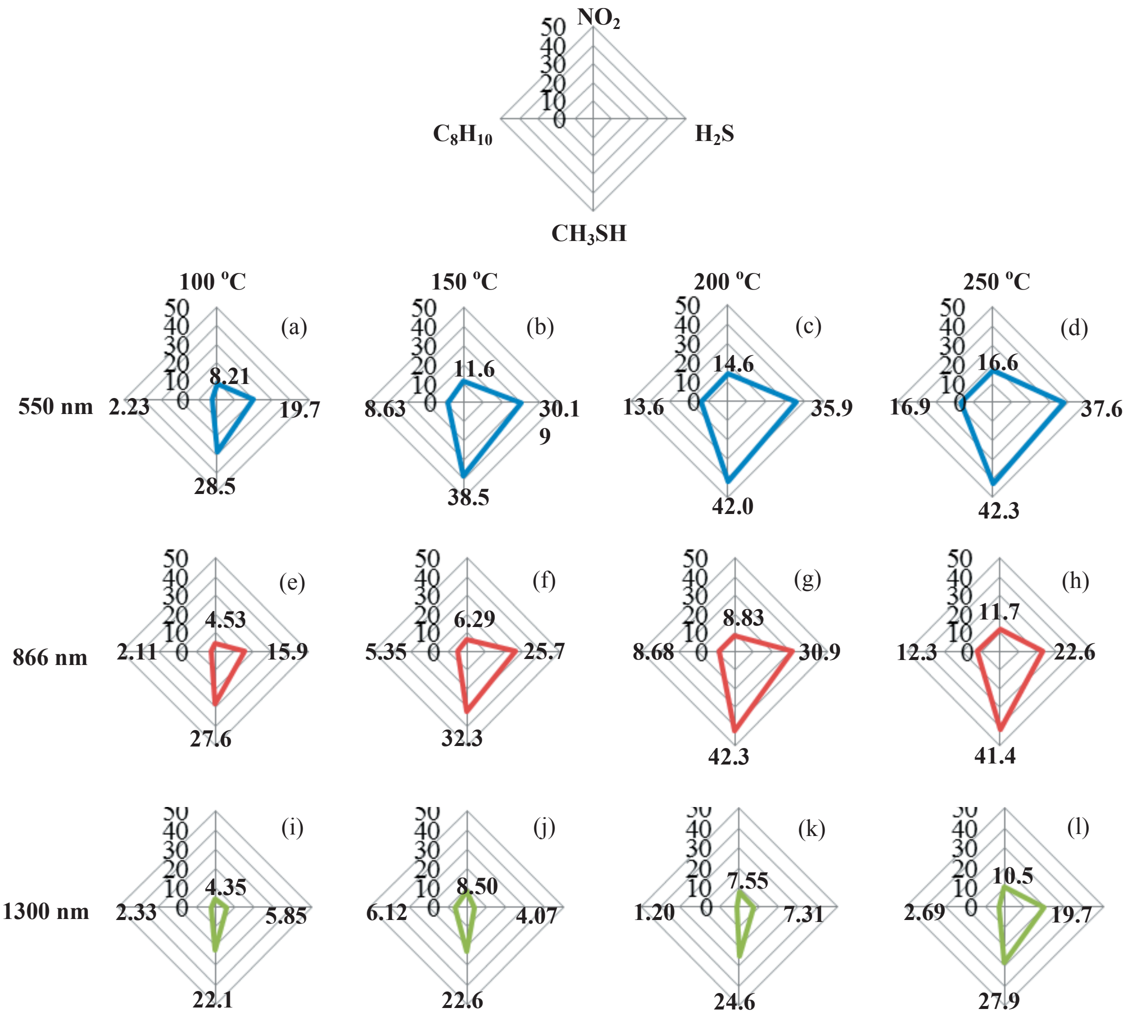

Fig. 8 The selectivity of MWCNTs array as resistance change.
(a) 550 nm, 100 °C; (b) 550 nm, 150 °C; (c) 550 nm, 200 °C; (d) 550 nm, 250 °C; (e) 866 nm, 100 °C; (f) 866 nm, 150 °C; (g) 866 nm, 200 °C; (h) 866 nm, 250 °C; (i) 1300 nm, 100 °C; (j) 1300 nm, 150 °C; (k) 1300 nm, 200 °C; (l) 1300 nm, 250 °C.

Acknowledgements

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