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Effects of the catalyst pretreatment on CO_2 sensors made by carbon nanotubes

C.S. Huang [a,b,*], B.R. Huang [c], C.H. Hsiao [a], C.Y. Yeh [b], C.C. Huang [b], Y.H. Jang [d]

[a] Department and Institute of Electronic Engineering, National Yunlin University of Science and Technology, Taiwan, 64002
[b] Graduate School of Optoelectronics, National Yunlin University of Science and Technology, Taiwan, 64002
[c] Graduate Institute of Electro-Optical Engineering, National Taiwan University of Science and Technology, Taiwan, 106
[d] Department of Materials Science and Engineering, National Chiao-Tung University, Taiwan, 300

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Abstract

A novel CO_2 sensor was made by carbon nanotubes (CNTs). The CNTs were synthesized by catalystic thermal chemical vapour deposition at 700 °C. Prior to the synthesis, the Fe catalysts were pretreated by H_2 plasma for different times. Two terminal resistance of the as-grown CNTs mat was measured under different CO_2 concentrations. It was found that without the catalyst pretreatment, the sensitivity was about 4% when the CNTs mat was exposed to 800 mTorr CO_2 concentration. However, with various catalyst pretreatment times of 5, 10, 15 and 20 min, the sensitivity was 3.69%, 6.27%, 9.54%, and 12.1%, respectively. The Raman spectroscopy showed the I_D/I_G decreased from 0.668 to 0.539 as the catalyst pretreatment time increased. The XPS also showed the correlation of surface chemical components with the Raman spectroscopy. The Fe catalyst H_2 plasma pretreatment affected both the graphitization and surface binding sites of CNTs.

Keywords: Catalyst; H_2 plasma; Carbon nanotubes; Sensor

1. Introduction

Gas monitoring is important in many circumstances such as manufacture processes and environmental protection. Traditional gas sensors made by using semiconducting oxides have to be operated at high temperature [1], and this limits the applications operated at the room temperature. In searching for new materials capable of operating at the room temperature, carbon nanotubes (CNTs) is the most promising candidate. Many researches [2–6] used the electrical properties of CNTs to carry out various gas sensors. The electrical resistance of CNTs was found to increase when exposed to reducing gas species (such as NH_3 [7], CO_2 [8,9], N_2 [10] and ethanol [11] etc.), but to decrease when exposed to oxidizing ones (such as O_2 [12] and NO_2 [13]).

CO_2, being one kind of greenhouse gas, has attracted some researches of CO_2 sensors on controlling industrial processes [14] and monitoring air quality [15]. In this paper, CO_2 sensors was made by CNTs with different catalyst pretreatments. The sensitivity showed great correlation with catalyst pretreatments. Raman and XPS spectroscopies suggested that graphitization of CNTs helped to increase the sensitivity.

2. Experimental details

A 16 nm Fe layer was deposited as catalysts on (100) *p*-type silicon substrate by RF sputtering with 150 W power and at 40 sccm Ar gas flow rate. Then, prior to the growth of CNTs, such catalyst-deposited samples were pretreated by H_2 microwave plasma for 5, 10, 15, 20 min, respectively. The microwave power was 700 W, with the work pressure of H_2 2 Torr and the temperature kept at 400 °C. Finally, CNTs were synthesized by the thermal CVD system at 700 °C N_2 was used as the carrier gas during the 60 min temperature rising process, at a flow rate of 100 sccm with 6.5 Torr. Reaching the 700 °C growth temperature, N_2 was switched off and C_2H_2 was

* Corresponding author. Chien-Sheng Huang, 123 University Road, Section 3, Douliou, Yunlin 64002, Taiwan. Tel.: +886 5 5342601; fax: +886 5 5312063.
E-mail address: huangchs@yuntech.edu.tw (C.S. Huang).

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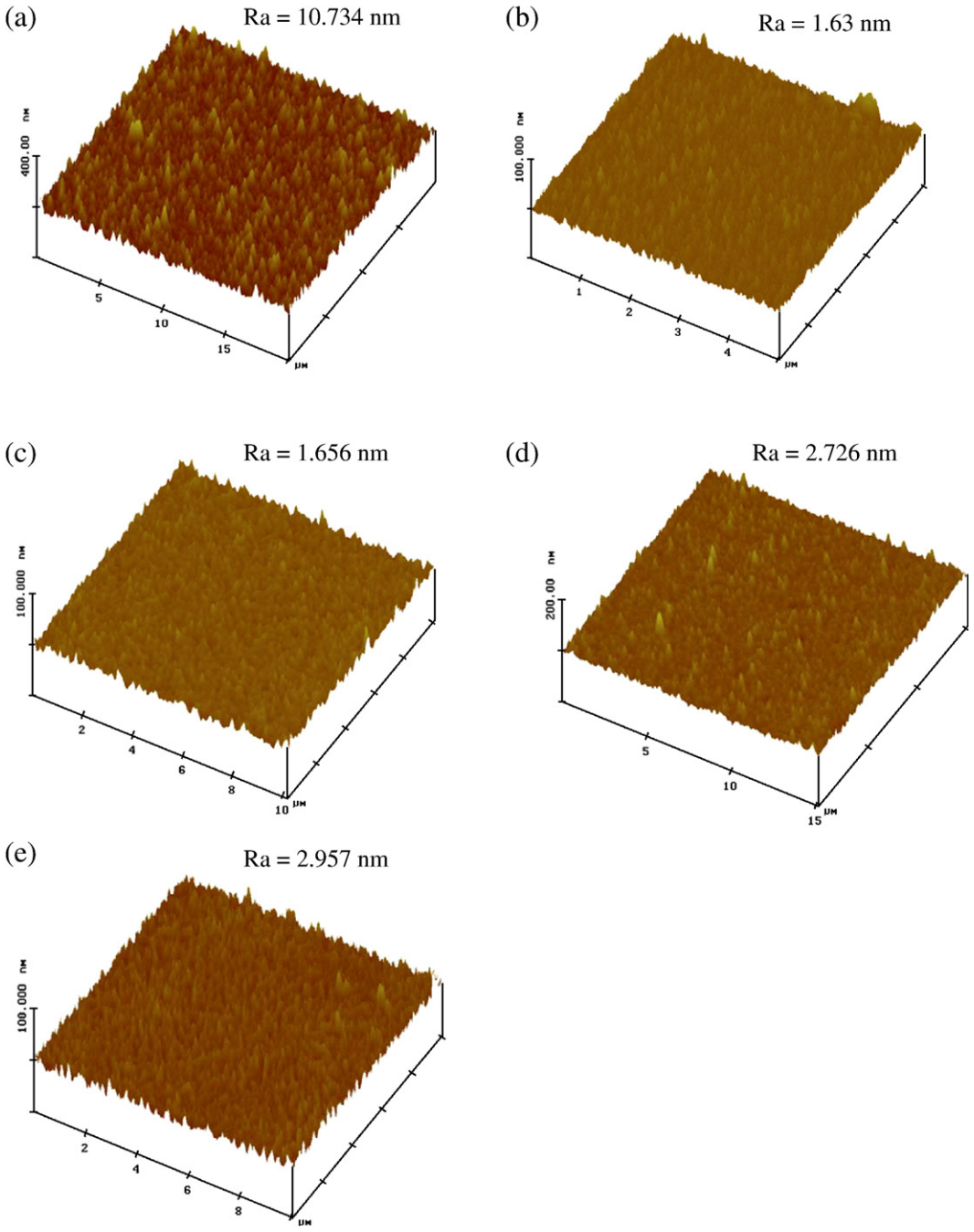

Fig. 1. AFM images of the Fe catalyst nano-film, (a) only 400 °C heating, (b)–(e) pretreated by H_2 plasma at 400 °C for 5, 10, 15, and 20 min, respectively.

switched on at a flow rate of 30 sccm with 3.5 Torr for 20 min. Then, C_2H_2 was switched off and the reactor was slowly cooled down to room temperature in N_2 ambient. As-grown CNTs mat was examined by Raman spectroscopy and X-ray photoemission spectroscopy (XPS) for the graphitization of sp^2 carbon bonding and surface chemical composition.

CO_2 sensing experiments were carried out by a high vacuum I–V measurement system. The resistance of various CNTs mats was measured under a series of CO_2 filling and pumping cycles, with the filling pressure from 50 mTorr to 800 mTorr. All experiments were conducted at room temperature.

3. Results and discussion

Fig. 1 showed the surface morphologies of Fe catalyst layer after H_2 plasma treatment for different time. Since the temperature was kept at 400 °C during the H_2 plasma treatment, one Fe catalyst-deposited sample, heating to 400 °C for 20 min without H_2 plasma, was shown in Fig. 1(a) for comparison. It was found that heating would make the Fe atoms aggregated, and the surface mean roughness R_a was 10.734 nm. As shown in Fig. 1(b), H_2 plasma treatment made the surface mean roughness decrease to 1.63 nm for 5 min treatment time. As treatment time increased to

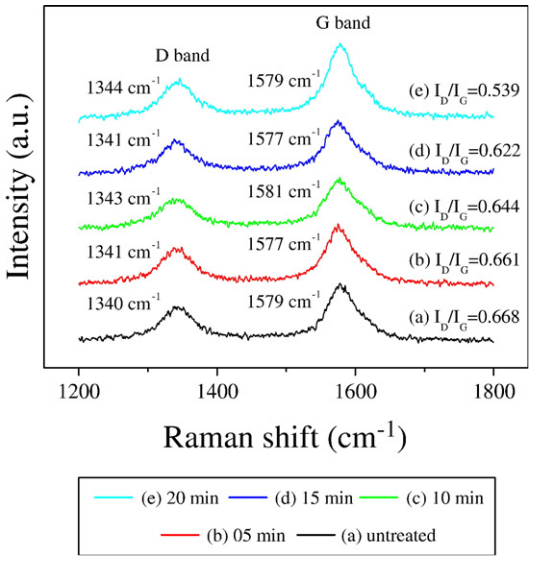

Fig. 2. The Raman spectra of as-grown CNTs mats, (a) without H_2 plasma and (b)–(e) pretreated by H_2 plasma at 400 °C for 5, 10, 15, and 20 min, respectively.

10, 15, 20 min, the surface mean roughness increased to 1.656, 2.726, 2.957 nm, respectively shown in Fig.1(c)–(e). Apparently, the effect of H_2 plasma was more than providing heat energy to the Fe catalyst nano-film [16]. The surface roughness of Fe catalyst nano-film had effects on the following growth of CNTs mat, e.g. the density and graphitization.

Fig. 2 showed the Raman spectra (taken with the 532 nm Nd: YAG laser line) of the CNTs mat. Both the typical D band (~1350 cm^{-1}) and G band (~1580 cm^{-1}) for multi-walled CNTs appeared [17]. The Lorentzian components fitting gave the peak values and the ratio I_D/I_G, which would be an graphitization index for CNTs. Smaller I_D/I_G ratio indicated high graphitic crystallinity of CNTs. Without H_2 plasma pretreatment, the I_D/I_G ratio was 0.668. As the H_2 plasma pretreatment time increased from 5, 10, 15 to 20 min, the I_D/I_G ratio decreased from 0.661, 0.644, 0.622 to 0.539, respectively. This also indicated that disordered carbon bonds decreased as the ratio decreased. Since there were plenty of oxygen and some

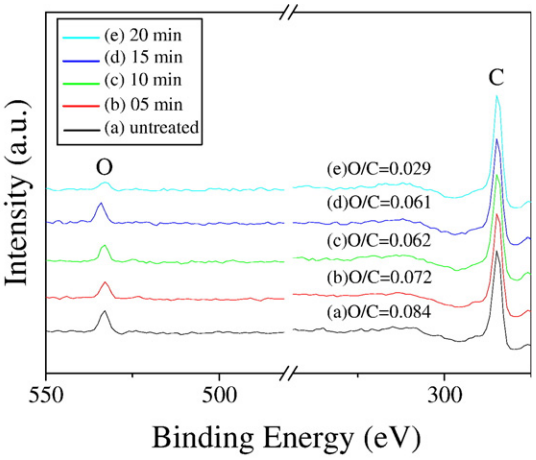

Fig. 3. XPS of as-grown CNTs mats, (a) without H_2 plasma and (b)–(e) pretreated by H_2 plasma at 400 °C for 5, 10, 15, and 20 min, respectively.

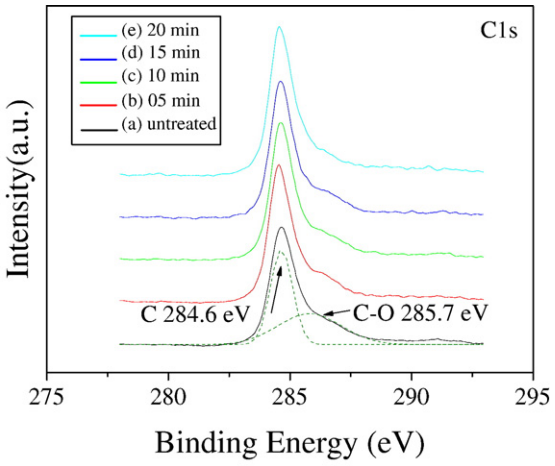

Fig. 4. XPS C1s spectra of as-grown CNTs mats, (a) without H_2 plasma and (b)–(e) pretreated by H_2 plasma at 400 °C for 5, 10, 15, and 20 min, respectively. The Gaussian fitting shows the C–O bonding at about 285.7 eV.

moisture in the air, the oxygenic contaminants were possibly found on the surface of as-grown CNTs mat. As the XPS shown in Fig. 3, without H_2 plasma pretreatment, the O/C ratio was 0.084. As the H_2 plasma pretreatment time increased from 5, 10, 15 to 20 min, the O/C ratio decreased from 0.072, 0.062, 0.061 to 0.029, respectively. The tendency was reasonable since the decrease of disordered carbon bonds reduced the chemiadsorption of oxygenic contaminants. The evidence of chemiadsorbed oxygenic contaminants was shown in Fig. 4, with the higher C1s binding energies which were recognized as C–O bonding (~285.7 eV).

Fig. 5 showed the resistance variations to time of as-grown CNTs mat upon exposure to a series of CO_2 filling and pumping cycles, with the filling pressure from 50 mTorr to 800 mTorr. Since as-grown CNTs were *p*-type and CO_2 were categorized as reducing species, the resistance CNTs mat would increase when exposing to CO_2 ambient [9]. Sensitivity (S) was defined as the ratio $S=[(R_{CO2}-R)/R]\times 100$, where R_{CO2} represented the CO_2-adsorbed saturated resistance of CNTs mat in CO_2 ambient during the filling half-cycle and R represented the resistance in pumping

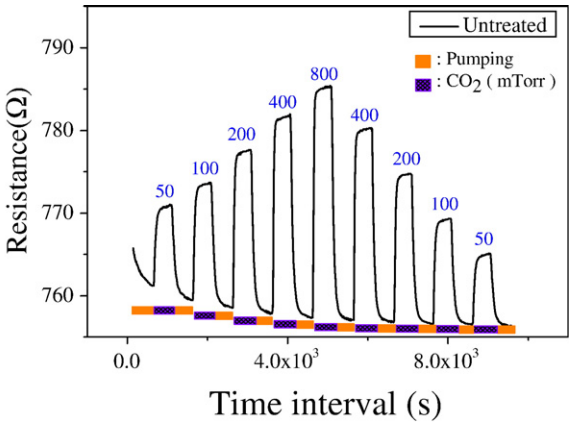

Fig. 5. The typical resistance variations to time of as-grown CNTs mat measured at room temperature under various CO_2 pressures, from 50 mTorr to 800 mTorr and back to 50 mTorr without H_2 plasma.

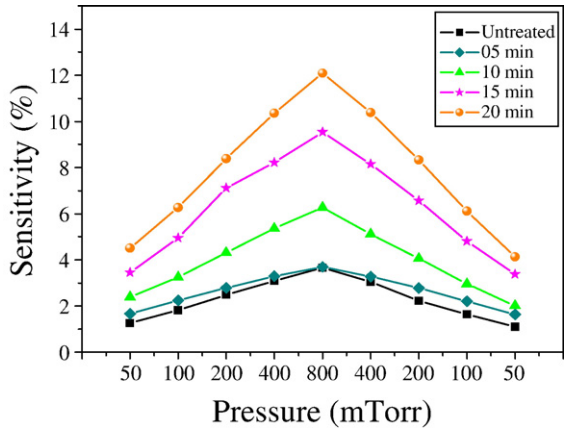

Fig. 6. The sensitivity S of as-grown CNTs mat, without H_2 plasma and pretreated by H_2 plasma at 400 °C for 5, 10, 15, and 20 min, respectively.

half-cycle. Fig. 6 showed the sensitivity calculated from Fig. 5. The sensitivity of CNTs mat without H_2 plasma pretreatment was 3.66% under 800 mTorr CO_2 concentration. After H_2 plasma pretreatment for 5 to 20 min, the sensitivity increased from 3.69% to 12.1% under 800 mTorr CO_2 concentration. The increase of sensitivity S seemed according to the graphitization of CNTs mats. There are four possible sites for adsorption on CNTs mat: internal (endohedral), interstitial channels, external groove sites, and external surfaces [18,19]. Since the CNTs mat was not packed compactly, the external surfaces of each CNTs played the major roles in the adsorption, and hence the sensitivity showed correlation with the graphitization and surface chemical of as-grown CNTs.

4. Conclusions

The Fe catalyst pretreatment by H_2 plasma has great effects on the graphitization and surface chemical compositions of as-grown CNTs. The sensitivity of CO_2 gas sensor made by CNTs was therefore affected.

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