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主 論 文 の 要 旨

論文題目　**A Study on the Fabrication of Highly Sensitive Hydrogen Sensor Based on Multiwall Carbon Nanotube Sheet**
（カーボンナノチューブシートを用いた高感度水素センサーの開発に関する研究）

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論 文 内 容 の 要 旨

With the development of hydrogen based applications, there is a rising necessity for hydrogen gas detection and monitoring. Because of its p-type semiconducting characteristic and extremely high surface-to-volume ratio, carbon nanotube (CNT) is considered to be an excellent candidate for hydrogen sensing. However, the complicated fabricating process and the random alignment in the fabricated CNT film limit the commercialization of CNT based hydrogen sensor. On the other hand, multiwall CNT (MWCNT) sheet is a MWCNT film in which MWCNTs are joined end-to-end structure and aligned nearly parallel. It can be easily prepared for meters by drawing from the spinnable MWCNT array and transferred without extra process such as dispersing CNT in organic solvents. Therefore, MWCNT sheet is a suitable choice for low-cost mass production of CNT based sensors. Besides, the high alignment and end-to-end entanglement of MWCNT sheet also offer more accessible sites for the gas molecules adsorption. This indicates that MWCNT sheet may show better gas sensing performance than ordinary MWCNT film.

In this study, we aimed at developing a hydrogen sensor based on MWCNT sheet with high sensing performance at room temperature. Two novel structures, i.e. the on-substrate multi-layer structure and the suspended cross-stacked structure, have been demonstrated in this research. Moreover, two-side Pd functionalization has been operated in order to improve the gas sensing performance of MWCNT sheet at room temperature. The conditions during spinnable vertical aligned CNT (VACNT) array synthesis, functionalization and stacking process have been investigated in order to achieve the optimal conditions for sensor fabrication. The relationship between the characteristic of MWCNT sheet and gas sensing performance has been evaluated in order to clarify the mechanism of the sensitivity improvement brought from the new structures. The details of this thesis are as follows:

Chapter 1 introduces the background of this research, which includes the importance of hydrogen detection, current situation of hydrogen sensors, advantages and limits of CNT based hydrogen sensors and the objectives of this study.

Chapter 2 presents the synthesis of spinnable VACNT array and the fabrication of MWCNT sheet. The conditions of chemical vapor deposition (CVD) process including the catalyst thickness, heating condition and gas flow ratio were investigated and the spinnability of the VACNT array were evaluated. It was found that faster heating rate and thinner Fe thickness lead to smaller size and higher density of the catalyst particles, which further results in better alignment of the CNT array. The optimal condition for the synthesis of spinnable array is as follows: 750 °C, 40 °C /min, (C_2H_4, H_2) = (80, 40) sccm, 1.2 nm Fe thickness. The MWCNT sheet was successfully drawn from the spinnable array in large scale with an outstanding repeatability. The fabricated MWCNT sheet obtains high purity and uniformity with a sheet resistance of 2739.7 Ω/□.

Chapter 3 reports a fabrication method of hydrogen sensor based on a stacking multi-layer structured MWCNT sheet. Various functionalizing conditions, sizes and numbers of the stacking layer were evaluated in the hydrogen sensing tests. Because of the reasonable distribution of Pd nanoparticles, the sample deposited with 3 nm Pd shows the highest response toward hydrogen. From the experimental results, layer dependence was found. When the layer number of stacked sheet increases from 1 to 3, the response at 4% H_2 increase from 5.75% to 12.31%. When continuing to stack more layers, the response hardly changes. This is because that the stacked layers fill in the space among CNTs and offer a better condition for the formation of groove sites. However, over-stacked layers also block the H_2 molecules from bottom-side CNTs due to too many layers. The sensor with 3 nm thickness of Pd and 3 layers of sheet shows the best hydrogen sensing performance with a response of 12.31% at 4% H_2 and a response time below 200 s.

Chapter 4 reports a novel suspended structure of cross-stacked MWCNT sheets for hydrogen sensing. The effects of suspended structure, cross-stacking process and two-side functionalization were investigated according to the results of gas sensing measurement. By hanging the sheet in the air, the surface area of the sheet is enlarged and a 106.5% higher response has been achieved comparing to the on-substrate sensor. By stacking the MWCNT sheets in mutually perpendicular directions, the MWCNTs are prevented from too close stacking which also enlarges the effective surface area for hydrogen sensing. Besides, because of the suspended structure, two-side functionalization becomes available, which further increases the response at the same

Pd thickness comparing to one-side functionalization. According to the gas sensing results, the sample with 2+1 layers and two-side 3 nm Pd deposition shows the highest response of 35.30% at 4% H_2.

Chapter 5 presents the summary of the most important conclusions achieved in this research. In conclusions, the novel MWCNT sheet based sensor demonstrated in this research shows the highest response among all the MWCNT based hydrogen sensors which have been reported in recent literatures. The method developed in this research is proved to be simple with convincing reliability. The new findings of this research point out a way for the mass production of the highly sensitive CNT-based sensors for the hydrogen detection at room temperature.