Improving the stability and reproducibility of the carbon nanotube gas ionization sensor by Co–Ti/Ti co-deposited catalyst layer

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ABSTRACT

A novel gas ionization sensor (GIS) of the carbon nanotube (CNT) film using the Co–Ti/Ti co-deposited catalyst layer had been proposed for the first time to exhibit higher stability and better reproducibility with respect to the CNT film ones with the single catalyst layer. For the proposed CNT GIS, the variation of the breakdown voltage (V_{br}) was less than 25% for the ten devices with the same structure measurement since the lengths of the CNT synthesized were uniform and aligned. Besides, the fluctuation of the V_{br} was about 14% during 1000 operation times in nitrogen at the pressure of 0.035 Torr. It was attributed to the adhesion between CNTs and the substrate could be improved since the co-deposited catalyst layer and Ti adhesion layer would be coalesced so that the Co nanoparticles would be partially immersed into Ti layer after hydrogen pretreatment. Such a CNT GIS with the co-deposited catalyst layer also exhibited high sensitivity and selectivity for different kinds of gases detection as well as the good linearity for detecting the gas mixture.

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1. Introduction

The sensing mechanism of the conventional semiconductor gas sensors based on the changes in the electrical properties of the semiconductor upon the exposure to gas. Since the same type gases exhibited the similar electrical properties, e.g. lower conductivities for all reducing gases and higher conductivities for all oxidizing gases, or vice versa. It cause that the gas sensor suffered from selectivity and reversibility issues [1–2]. Gas ionization sensors (GISs) had been introduced to overcome these problems because GISs could fingerprint the ionization characteristics of distinct gases. However, GISs were limited by the huge and bulky vacuum tube architecture, risky high-voltage operation, and high power consumption.

Carbon nanotubes (CNTs) with high aspect ratio had attracted considerable attention in the fabrication of GIS because they could generate very high electric fields at relatively low voltages [3–5]. However, CNTs could be degraded easily under the high electric current as a light element nanostructure [6]. So some other kind of one-dimensional (1D) nanomaterials such as ZnO, Au nanostructures were also used for gas ionization sensor to enhance the stability of the sensor [7,8]. But these kinds of instruments still

had high power consumption and risky high-voltage operation, and thus could not be used on site.

According to the previous research [9], the co-deposited catalyst layer could improve the reliability and uniformity of the CNTs as the emitters for the application in the field emission devices. However, the CNTs synthesis with the co-deposited layer as the cathode was never demonstrated for the application in the GIS.

In this letter, the CNTs synthesis with the co-deposited catalyst layer had been utilized for the first time to fabricate a GIS. Compared to the CNT GIS with the single catalyst layer, the proposed CNT ones exhibited the superior gas ionization characteristics, including higher stability and better reproducibility. The gas ionization characteristics of such a CNT GIS for different kinds of gases detection were also investigated.
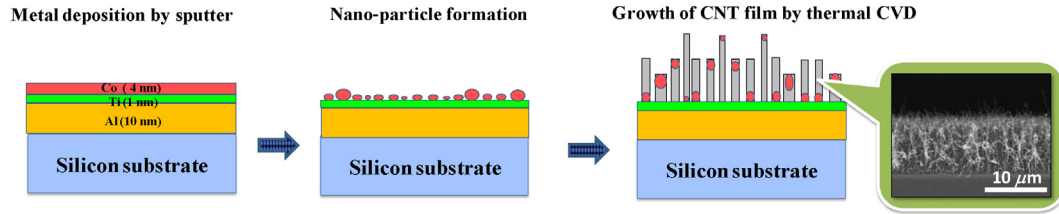
2. Experimental

2.1. Fabrication of the conventional and proposed CNT GISs

Flowcharts of the formation for the CNT film with the single catalyst layer and the co-deposited catalyst layer were shown in Fig. 1. At first, a 4 inch (100) p-type wafer was cleaned by the standard RCA cleaning process. The 10-nm-thick aluminum (Al) and 1-nm-thick titanium (Ti) as the supporting and adhesion layer, respectively, were sequentially deposited on the Si substrate through the magnetron sputtering system at room temperature. Then two different samples, the conventional sample as the reference and
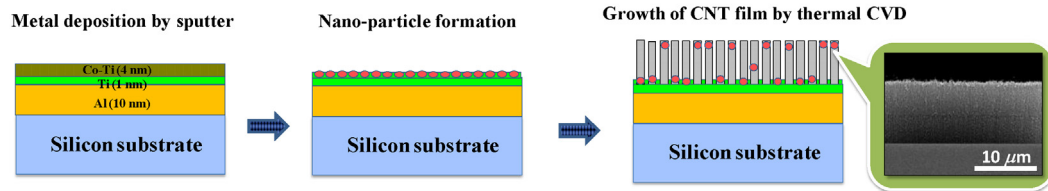
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Conventional sample: single catalyst layer (Co)

Metal deposition by sputter   Nano-particle formation   Growth of CNT film by thermal CVD

Proposed sample: co-deposited catalyst layer (Co-Ti)

Metal deposition by sputter   Nano-particle formation   Growth of CNT film by thermal CVD

Fig. 1. Flowcharts of the formation for the CNT films with the single catalyst layer and the co-deposited catalyst layer (inset were the FE-SEM images of CNT synthesis for both samples).

the proposed one, were prepared for comparison. For the conventional sample, a 4-nm-thick cobalt (Co) layer was deposited on the Ti adhesion layer as the catalyst layer through the magnetron sputtering system. For the proposed sample, the Co catalyst layer of the conventional sample was replaced by the Co–Ti co-deposited layer. The Co and Ti were co-deposited by the magnetron sputter system as a novel catalyst layer on the Ti adhesion layer with weight percentage of 75% for Co and 25% for Ti. Besides, the quantity of Co

was the same for the conventional sample. Both samples were then loaded into thermal CVD. The catalyst metal was pretreated with the hydrogen at 600 °C for 5 min under the hydrogen flow rate at 300 sccm to transfer it as nano-particles [10]. Then, the CNT films were grown at 700 °C under the hydrogen, nitrogen, and ethylene flow rates at 300 sccm, 500 sccm, and 100 sccm. The length of CNTs was controlled to be 10 μm by tuning the synthesized time. The SEM images of the CNT synthesis were shown in Fig. 1. That
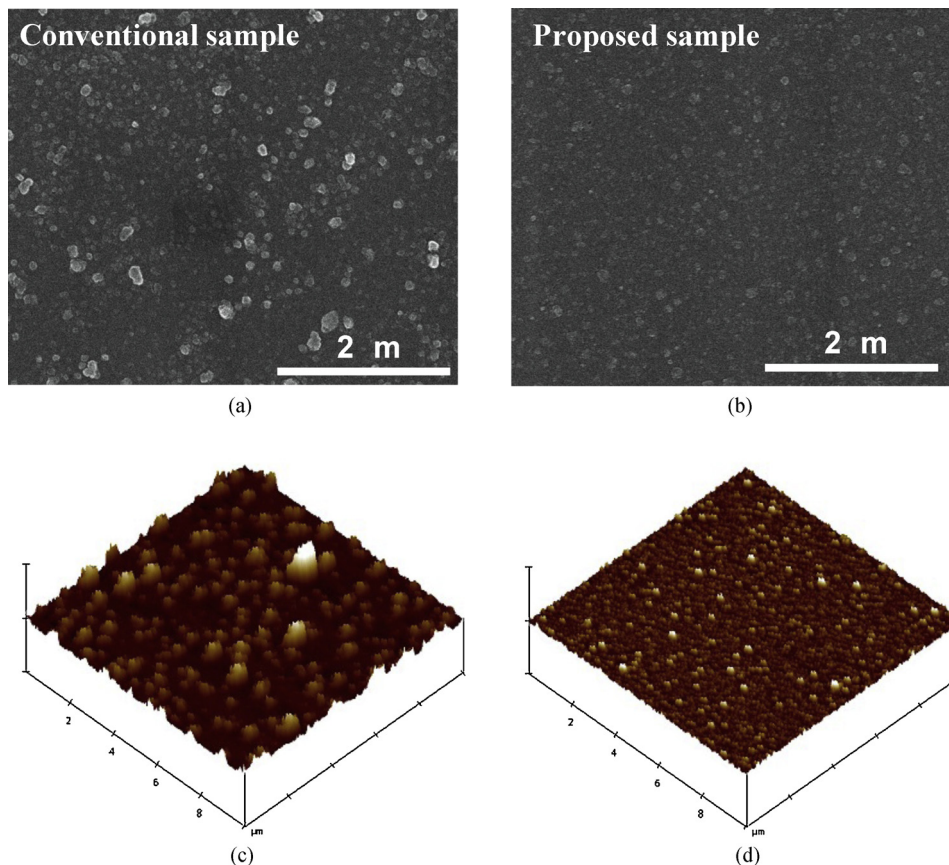
Fig. 2. FE-SEM images of the catalyst nanoparticles for (a) the conventional sample and (b) proposed sample; and AFM images of the catalyst nanoparticles for (c) the conventional sample and (d) proposed sample.

exhibited the disordered and aligned CNTs for the conventional sample and proposed sample, correspondingly. The micrographs of the catalyst nanoparticles for the conventional sample and proposed sample were shown in Fig. 2(a) and (b), respectively, after being pretreated in hydrogen ambient at 600 °C for 5 min in the thermal-CVD. The catalyst nanoparticles in the conventional sample had larger average diameter and variation of diameter than those in the proposed sample. Additionally, the atomic force microscope analysis was also applied to observe the nanoparticles in both the conventional and the proposed samples and the results were shown in Fig. 2(c) and (d), correspondingly. A more uniform distribution of catalyst nanoparticles with smaller variation of diameter was also observed in the proposed sample as compared with the catalyst nanoparticles in the conventional sample. It was attributed to the suppression of coalescence of the Co nanoparticles in the co-deposited Co–Ti film after hydrogen pretreatment and therefore the length variation of the CNTs synthesized was also remarkably suppressed. Moreover, the catalyst nanoparticles in the conventional sample were so non-uniform that the van der waals forces were different between CNTs during the growth of CNTs. It was the reason why the disorder CNTs were exhibited in the conventional sample.

2.2. The measuring system of gas ionization sensor

An indium tin oxide was utilized as the anode and the CNTs acted as the cathode. A distance d of 300 μm was kept between the anode and the tip of the CNTs. During the measurement, the sample was loaded into a vacuum chamber and the breakdown voltage (V_{br}) was measured in the target gas environment under different gas pressure. The anode voltage was applied with a source measurement unit (Keithley 237) while the cathode was biased at 0 V (Keithley 238).

3. Results and discussion

3.1. Gas ionization characteristics

Fig. 3(a) and (b) showed the gas current–voltage (I–V) characteristics of the conventional sample and proposed sample in nitrogen under different gas pressures, accordingly. The gas pressure was varied from 1.3×10^{-3} to 2.6×10^{-1} Torr. The V_{br}'s of the both samples were relatively high at low gas pressure and then decreased to a minimum value as the gas pressure increased to 0.035 Torr. As the gas pressure was larger than 0.035 Torr, the V_{br}'s increased with increasing the gas pressure. It was worth noting that the current of the conventional sample were unstable at the low or high gas pressures. That could be attributed to the non-uniform distribution of the electric field since the lengths of the CNT synthesis were disordered. On the other hand, due to the lengths of the CNT synthesized in the proposed sample were uniform and aligned, the current were stable under different gas pressures.

3.1.1. Reproducibility

To further investigate the influence of the CNT synthesis with co-deposited catalyst layer on the reproducibility of the gas ionization characteristics, the ten devices of the both different samples were measured in nitrogen under different gas pressures. The V_{br}'s as a function of the product of gas pressure, p, and distance between the anode and the tip of the CNTs, d, for the both samples were shown in Fig. 3(c). It was observed that the similar trends of V_{br} curves were obtained for the both samples. Moreover, the V_{br}'s had the minima as the $p \times d$ approached 10^{-2} Torr-cm (i.e., the gas pressure was equal to 0.035 Torr at the fixed d of 300 μm). From the Paschen's law, the relationship between the V_{br} curve and
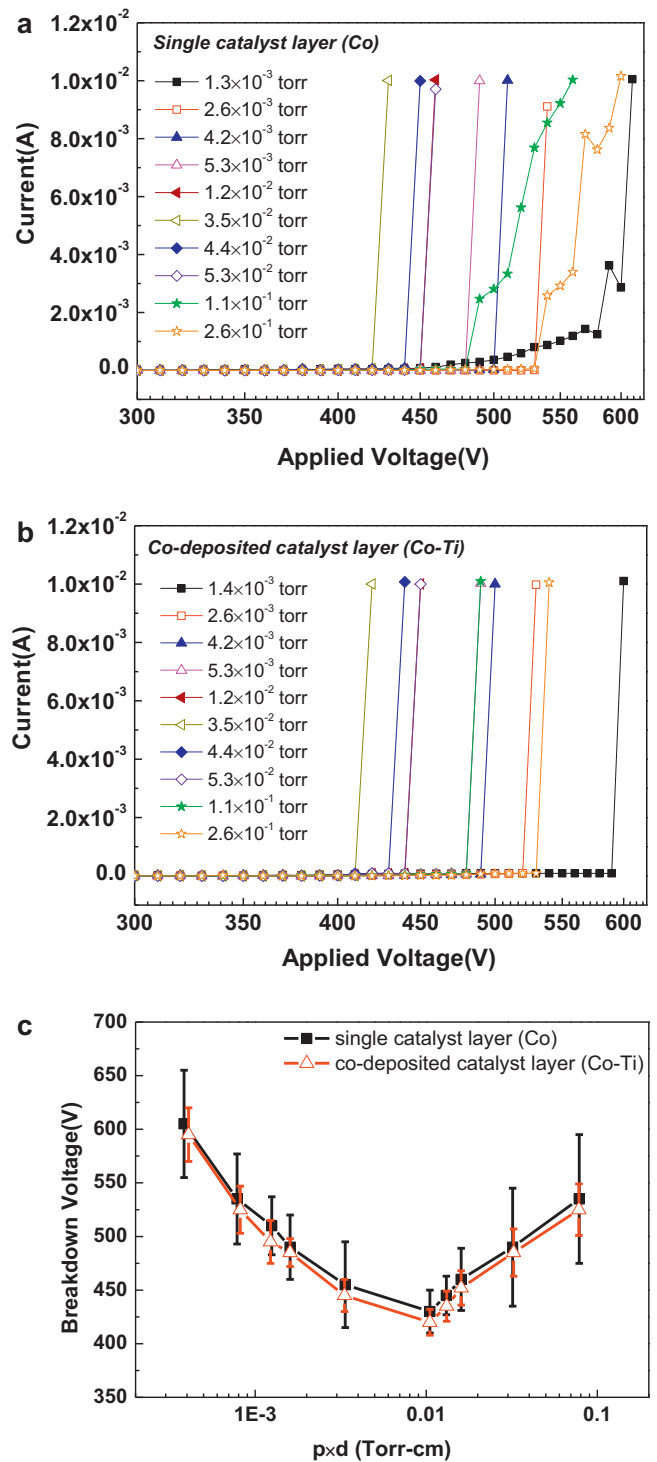

Fig. 3. Gas ionization characteristics of both samples: (a) gas I–V characteristics for the conventional sample (b) gas I–V characteristics for the proposed sample (c) V_{br}'s as a function of the $p \times d$ for both samples for ten devices measurement.

the $p \times d$ was dependent on the test gas. Since the testing gas was nitrogen for the both samples, the trends of V_{br} curves should be similar. In addition, the variations of the V_{br}'s were less than 60% and 25% with respect to the conventional and proposed samples for the ten devices measurement. It was reflected that the proposed sample had better reproducibility than the conventional sample since the CNT synthesis of the proposed sample were uniform and aligned.
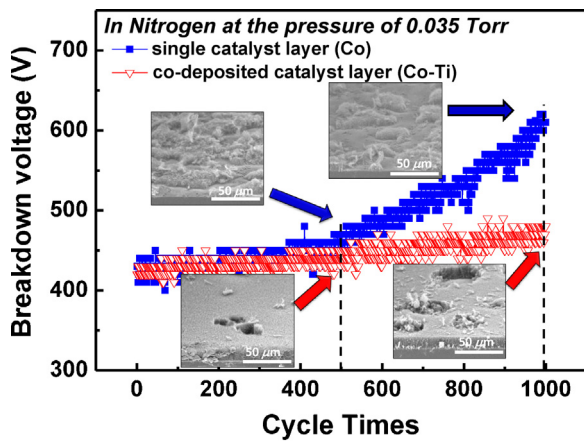
Fig. 4. Fluctuation of the V_{br} for both samples in nitrogen at the pressure of 0.0035 Torr after 1000 time-continuous breakdown (inset were the FE-SEM images of both samples after 500 and 1000 cycle times).

3.1.2. Stability

Subsequently, the stabilities of both samples were tested and compared. The breakdown phenomena were generated continuously 1000 times in nitrogen at 0.0035 Torr as shown in Fig. 4. The fluctuation of the V_{br} for the proposed sample was about 14%, while the V_{br} of the conventional sample increased with the increase of time and ended up at 42% of the initial value. To find

the reason for this phenomenon, the morphologies of both samples after continuous breakdown were observed by SEM, as shown in the inset of Fig. 4. Obviously, some CNTs were pulled off from the substrate and others CNTs were burnt away when the conventional sample was measured after 500 times. After 1000 measurement times, the phenomena were seriously revealed in the figure. Those phenomena resulted from the dipole generation as the electric field between two electrodes was increased and the Joule heating effect as the devices with a high current density passing through. Those were attributed to a poor adhesion between CNTs and the substrate [11]. On the other hand, the pull off and evaporation of CNTs in the proposed sample were improved. This is ascribed to the adhesion between CNTs and the substrate could be improved since the co-deposition catalyst layer and Ti adhesion layer would be coalesced so that the Co nanoparticles would be partially immersed into Ti layer after hydrogen pretreatment [9]. Therefore, the stabilities of the propose sample was better than those of the conventional sample.

3.2. Single gas and gas mixture detection

Furthermore, the conventional and proposed CNT GIS were used to distinct the different gases and detect the gas mixture at the pressure of 0.035 Torr. The I–V characteristics of both conventional and proposed CNT GIS for five single gases were shown in Fig. 5(a) and (b), respectively. From Fig. 5(a) and (b), the gas variety could be identified. Moreover, Argon (Ar) gas displayed the lowest V_{br} and
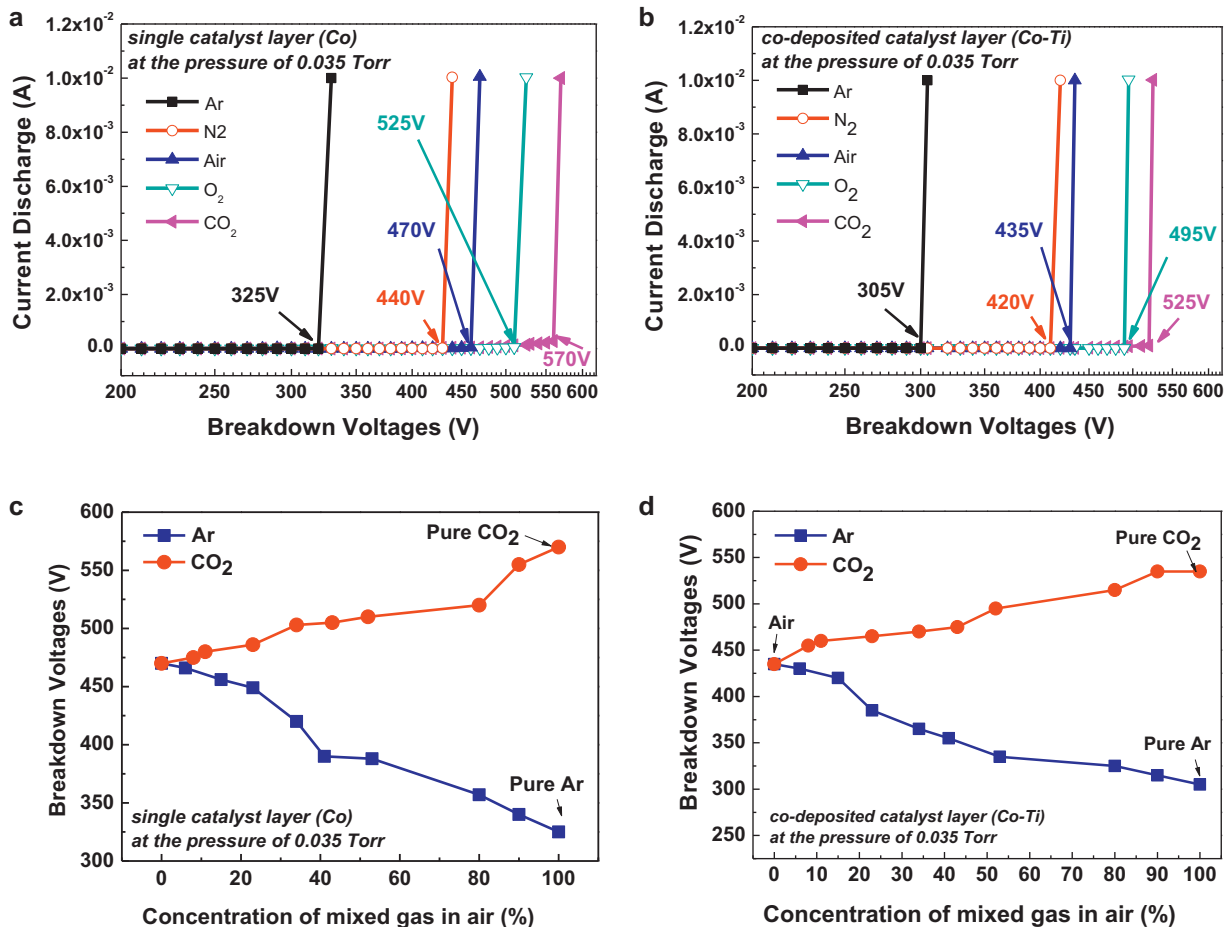

Fig. 5. Gas I–V characteristics for the five single gases at the pressure was 0.035 Torr for (a) the conventional sample and (b) proposed sample; and V_{br}'s of Ar–air and CO_2–air gases in mixture as a function of gas concentration as the pressure was 0.035 Torr for (c) the conventional sample and (d) proposed sample.

carbon dioxide (CO_2) gas showed the highest V_{br}. Although the V_{br} depended mainly on the intensity of electric field and the bonding energy of the gas molecules [12], the numerical order of the V_{br} among the detected gases would be influenced by the selection of the $p \times d$ value. Therefore, it caused that the numerical order of the V_{br} were shown as Ar < N_2 < Air < O_2 < CO_2 in this manuscript. Besides, the V_{br}'s of five single gases in the conventional sample were larger than those in the proposed sample. It should be attributed to the inaccuracy of the selected sample since the conventional sample has large variation of the GIS performance. Fig. 5(c) and (d) shows the V_{br} of Ar–air and CO_2–air gases in mixture as a function of gas concentration for the conventional sample and proposed sample, correspondingly. Obviously, the V_{br} increased with increasing CO_2 concentration. In contrast, the V_{br} decreased with increasing Ar concentration. This was because air had a higher V_{br} than Ar and lower V_{br} than CO_2, so the presence of air molecules tended to impede the breakdown of Ar and assist the breakdown of CO_2. It was worth noting that two cases in the proposed sample exhibited the better linearity as compared with those in the conventional sample. It should be imputed to the worse stability for the conventional sample. Furthermore, both two cases in the proposed sample exhibited the good linearity to compare with previous researches [3,4]. The experimental results showed that the proposed CNTs film was more effective for the application in GIS.

4. Conclusion

The superior ionization characteristics of the CNT GIS had been proposed for the first time with the Co–Ti/Ti co-deposited catalyst layer to exhibit higher stability and better reproducibility with respect to the CNT film ones with single catalyst layer. For the proposed CNT GIS, the variation of the V_{br} was less than 25% for the ten devices with the same structure measurement since the lengths of the CNT synthesized were uniform and aligned. Besides, the fluctuation of the V_{br} was about 14% during 1000 operation times in nitrogen at the pressure of 0.035 Torr due to the better adhesion between CNTs and the substrate. Such an optimum GIS with the CNT pillars also exhibited high sensitivity and selectivity for different kinds of gases detection as well as the good linearity for detecting the gas mixture.

Acknowledgments

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