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Effect of arrangement of carbon nanotube pillars on its gas ionization characteristics

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ABSTRACT

The gas ionization sensors (GISs) using the carbon nanotube (CNT) pillars which has the pillar height (H) of 15 μm with interpillar spacing (R) of 30 μm as the cathode had been proposed for the first time to exhibit the 20 times higher field enhancement factor (β) and the lower breakdown voltage of 350 V with respect to the CNT film ones for nitrogen gas at the pressure of 0.035 Torr. As the H increased from 5 μm to 15 μm, the β increased with increasing the H since the electrical field could be enhanced via the aspect ratio increment. However, as the H increased from 15 μm to 60 μm, the β decreased with increasing the H owing to the increased field-screening effect. 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.

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 exhibit the similar electrical properties, e.g. lower conductivities for all reducing gases and higher conductivities for all oxidizing gases, or vice versa. It caused that the gas sensors suffered from selectivity and reversibility issues [1]. 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.

One-dimensional (1D) nanomaterials 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 [2–7]. Among all 1D nanomaterials, carbon nanotubes (CNTs) were extensively owing to their relatively low work function, very sharp nanotips, and structural and chemical stability [4–7]. According to the previous research [4], the nanomaterial density effect on the field enhancement (FE) behavior played an important role to improve the gas ionization characteristics because the FE characteristics of CNTs might be influenced by the field-screening effect from the proximity of neighboring CNTs. However, it was very difficult to exactly control the intertube distance for the CNT film. Therefore, it implied that the ratio of CNT height to intertube distance on the FE characteristics for the CNT films was very hard to be empirically realized. In recent years, the CNT pillars had been widely adopted for the field emission devices. The long and vertically aligned pillars with the exact control of the interpillar spacing (R) could be therefore practiced. However, the CNT pillars as the cathode were never demonstrated for the application in the GIS.

In this letter, the CNT pillars had been utilized for the first time to fabricate a GIS. As compared with the CNT film GIS, the CNT pillar ones exhibited the superior gas ionization characteristics, including sensitivity and selectivity for different kinds of gases detection as well as the linearity of the gas mixture. The pillar height effect of such CNT pillar GISs was also investigated.

2. Experiment

2.1. Fabrication of CNT pillar and film

At first, a 4 in. (1 0 0) p-type wafer was cleaned by the standard RCA cleaning process. Afterward, a photoresist was spin-coated on the Si substrate and the catalytic layer was defined by the mask which has the 50-μm-diameter circles with interspacing of 30 μm by photolithography. The 10-nm-thick aluminum, 1-nm-thick titanium, and 4-nm-thick co-deposition cobalt–titanium as the supporting, adhesion, and catalytic layers, respectively, were sequentially deposited on the photoresist-patterned Si substrate

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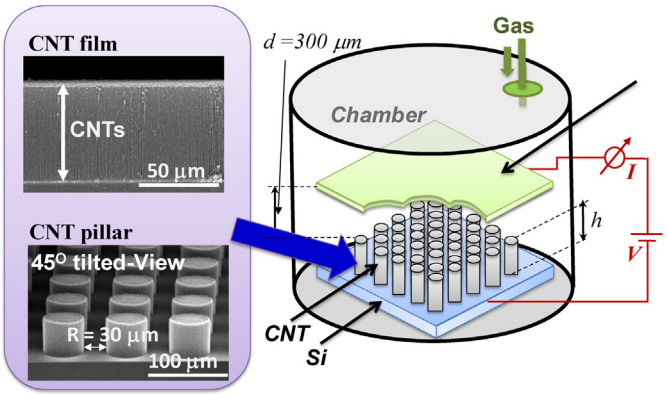

Fig. 1. Measurement setup of the gas ionization sensor. (Insets were FE-SEM images at the height of 60 μm: cross-sectional image of the CNT film and 45° tilted-view image of the CNT pillars.

through the magnetron sputtering system at room temperature. Then, the patterns were formed after removing the photoresist by lift-off method. Finally, the CNT pillars were grown on the patterned catalyst by the thermal CVD. The height of CNTs pillars were controlled to be 5, 10, 15, and 60 μm, accordingly, by tuning the synthesized time. Therefore, the diameter and the *R* of the CNT pillars were set as 50 μm and 30 μm, respectively. For comparison, the CNTs films with the same catalytic metal layers but unpatented were also performed as the gas ionization sensor. The FE-SEM images exhibited the long vertically aligned CNTs for both the pillars and films, as shown in the inset of Fig. 1. Besides, the *R* of the CNT pillars could be precisely controlled.

2.2. The measuring system of gas ionization sensor

The gas ionization measurement setup was depicted in Fig. 1. An indium tin oxide was utilized as the anode and the CNT pillar or films acted as the cathodes. A distance *d* of 300 μm was kept between the anode and the tip of the CNTs for all measurements of various CNT structures. During the measurement, the sample was loaded into a vacuum chamber and the breakdown voltage (V_{br}) was measured in the target gas environment at different gas pressures. 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. 2(a) shows the V_{br} as a function of the product of gas pressure, *p*, and distance between the anode and the tip of the CNTs, *d*, for the CNT films and pillars with different heights in nitrogen. The gas pressure was varied from 1.3×10^{-3} to 2.5×10^{-1} Torr. From Fig. 2(a), the CNT films exhibited only one curve since the *d* was fixed as 300 μm. It was observed that the similar trends of V_{br} curves were obtained for not only the CNT films but also the CNT pillars with different heights. From the Paschen's law, the relationship between the V_{br} curve and the $p \times d$ was dependent on the test gas. Since the testing gas was nitrogen, the trends of V_{br} curves should be similar for all CNT samples. But the CNT pillars with different heights exhibited different V_{br}'s for the same $p \times d$. As the pillar height (*H*) increased from 5 μm to 15 μm, the V_{br} curve decreased with increasing the *H*. However, as the *H* increased from 15 μm to

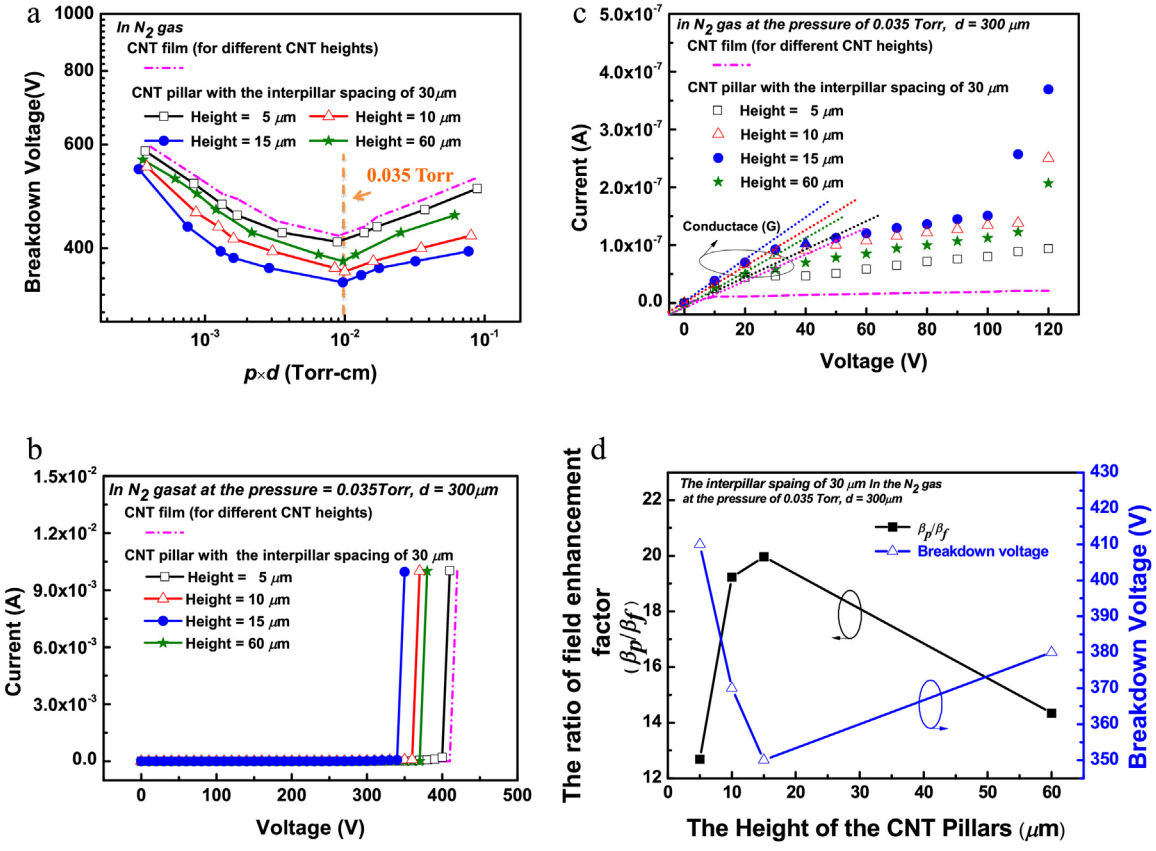

Fig. 2. Gas ionization characteristics at the pressure of 0.035 Torr in nitrogen: (a) V_{br} as a function of the $p \times d$ for the CNT film and different pillar heights. (b) Gas *I*–*V* characteristics for the CNT film and different pillar heights. (c) Pre-breakdown characteristic of the CNT film and pillars with different pillar heights. (d) β_p/β_f and V_{br} as a function of the height of the CNT pillars.

60 μm, the V_{br} curve increased with increasing the H. 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).

To further realize the V_{br} variation with the different H, the gas pressure for the lowest breakdown voltage, namely 0.035 Torr, was therefore adopted. The current–voltage (I–V) characteristics for all the GISs in nitrogen gas at the gas pressure of 0.035 Torr were shown in Fig. 2(b). The V_{br}'s of the CNT pillar GISs were 410, 370, 350, and 380 V for the H of 5, 10, 15, and 60 μm, respectively. In contrast, the V_{br} of the CNT film ones was 420 V. Therefore, the proposed CNT pillar GISs exhibited the better characteristics than the CNT film ones. Furthermore, the structure of the CNT pillars with the H of 15 μm had the lowest V_{br} in all CNT pillars with different heights. It was conjectured the influence of the H on the FE characteristics of the CNT pillars GIS.

3.2. Field enhancement effect of the cathode CNT pillars and their aspect ratio

Consequently, the FE factors of all CNT GISs were further discussed. Fig. 2(c) shows the pre-breakdown characteristics of GISs for the CNT films and pillars with different heights. In addition, the effective conductance G of the devices could be determined by the slope of the ohmic region of the I–V characteristics, as the dash dot in Fig. 2(c). It was evident that all the effective conductance of the CNT pillar GISs, G_p, were higher than the CNT film ones, G_f. Moreover, the CNT pillar GIS with the H of 15 μm had a maxima effective conductance among all CNT pillar ones.

For the typical gas I–V characteristic, the current density was determined by the carriers travel speed as the electric field was very small and could be therefore expressed as [7]

$$J = \sigma_{gas} E_{eff} = \sigma_{gas} \beta E_{app} \quad (1)$$

where σ_{gas} was the gas conductivity, E_{eff} was the effective enhanced field at the tip vicinity, and E_{app} was the applied electric field between the electrodes. According to Eq. (1), the current densities in the CNT film and pillars could be obtained as

$$J_f = \sigma_{gas} \beta_f E_{app} \text{ and } J_p = \sigma_{gas} \beta_p E_{app}, \quad (2)$$

where J_f and J_p were the current density of the CNT film and pillars, as well as β_f and β_p were the FE factor of the CNT film and pillars. Since all of the devices were examined in the same chamber for the same test gas, so the σ_{gas} would be the same. Then, the ratio of the J_p and J_f could be written as

$$\frac{J_p}{J_f} = \frac{\beta_p}{\beta_f} \quad (3)$$

From the ratio of the G_p and G_f could be written as the

$$\frac{G_p}{G_f} = \frac{I_p/V_p}{I_f/V_f} = \frac{J_p A_p/E_{app} d}{J_f A_f/E_{app} d} = \frac{\beta_p}{\beta_f} \times \frac{A_p}{A_f}, \quad (4)$$

where A_f and A_p were the areas for the CNT film and CNT pillars, respectively. As a result, the β_p/β_f were equal to the G_p/G_f owing to the $A_f \approx A_p$. Fig. 2(d) shows the β_p/β_f and the V_{br} as a function of the H at the pressure of 0.035 Torr in nitrogen. The β_p/β_f of the CNT pillars were about 12.5, 19, 20, and 14.5 V with respect to the H of 5, 10, 15, and 60 μm. As the H increased from 5 μm to 15 μm, the β increased with increasing the H since the electrical field could be enhanced via the aspect ratio increment. However, as the H increased from 15 μm to 60 μm, the β decreased with increasing the pillar heights owing to the increased field screening effect. Therefore, the β_p/β_f exhibited the maximum at the H of 15 μm. By the way, the V_{br} had thus a minimum at the H of 15 μm for the R of 30 μm.

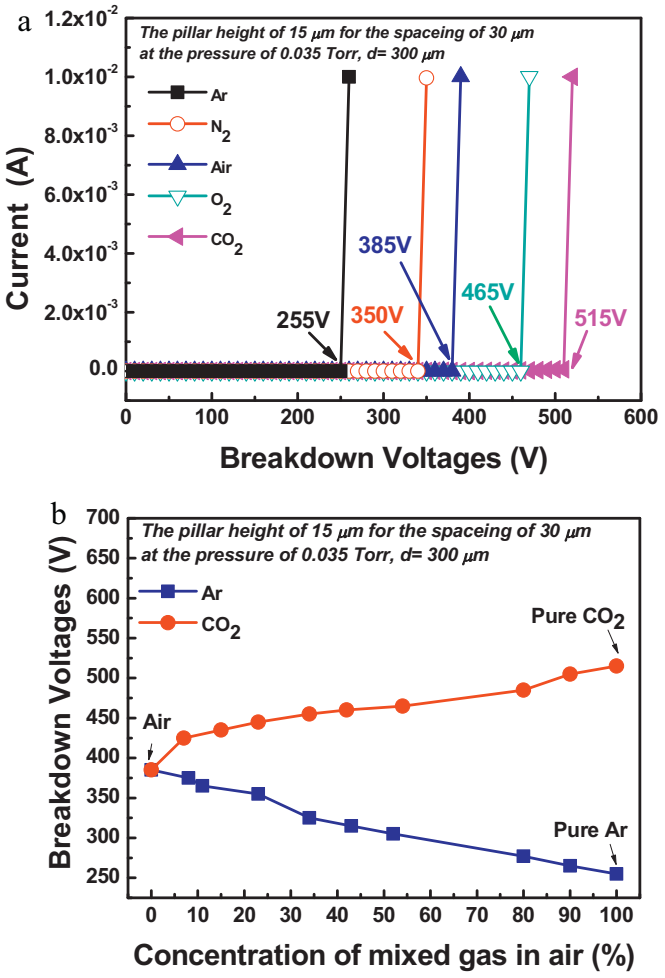

Fig. 3. (a) Gas I–V characteristics of the CNT pillars at the H of 15 μm for the five single gases as the pressure was 0.035 Torr. (b) V_{br} of Ar-air and CO_2-air gases in mixture as a function of gas concentration as the pressure was 0.035 Torr.

3.3. Single gas and gas mixture detection

Furthermore, the optimal CNT pillar GIS, which was at the H of 15 μm and the R of 30 μm, was used to distinct the different gases and detect the gas mixture at the pressure of 0.035 Torr. The I–V characteristics of the CNT pillar GIS for five single gases are shown in Fig. 3. From Fig. 3(a), the gas variety could be identified. Moreover, Argon (Ar) gas displayed the lowest V_{br} of 255 V and carbon dioxide (CO_2) gas showed the highest V_{br} of 515 V. Although the V_{br} depended mainly on the intensity of electric field and the bonding energy of the gas molecules [8], the numerical order of the V_{br} of 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 (225 V) < N_2 (350 V) < air (385 V) < O_2 (465 V) < CO_2 (515 V) in this manuscript. Fig. 3(b) shows the V_{br} of Ar-air and CO_2-air gases in mixture as a function of gas concentration. 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. Both two cases exhibited the good linearity to compare with previous researches [5,6]. The experimental results showed that the optimum arrangement CNT pillars were more effective for the application in GIS.

4. Conclusion

The superior ionization characteristics of the GIS had been proposed for the first time via the vertical-aligned CNT pillars as the cathode to exhibit the 20 times higher β and the lower V_{br} of 350 V for the H of 15 μm and the R of 30 μm with respect to the CNT film ones for the nitrogen gas at the pressure of 0.035 Torr. As the H increased from 5 μm to 15 μm, the β increased with increasing the H since the electrical field could be enhanced via the aspect ratio increment. However, as the H increased from 15 μm to 60 μm, the β decreased with increasing the pillar heights owing to the increased field screening effect. 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.

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