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Selectivity modification of graphene-based ammonia gas detection by the substrate treated with CF_4 plasma

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Abstract

The fluorinated silicon nitride worked as substrate by using CF_4 plasma is investigated the gas sensing performance of monolayer graphene. The response of nitrogen dioxide (NO_2) of graphene sensors was decreased with increasing fluorination time. The maximum NH_3-reponse of 28.8% and the minimum NO_2-response of 7.5% were achieved in the graphene with CF_4 plasma for 6 min on silicon nitride. The enhancement of ammonia-selectivity could be from the polar dipole (F-N) formation in silicon nitride due to the incorporation of fluorine by CF_4 plasma treatment.

1. Introduction

Ammonia (NH_3) in the human breath is a critical marker for noninvasive diagnosis of liver cirrhosis [1]. Ammonia is also a toxic compound. Even a ppm level exposure to ammonia, it can irritate a respiratory tract. Therefore, the ammonia detection at low concentrations is importance for human health. Graphene is a better candidate in sensor devices because this two dimensional structure with one atom thickness allows a full exposure and adsorbs of gas molecules down to ppb level [2]. However, the poor selectivity was a challenge for graphene gas sensor in practical applications [2]. Hence, some researches were proposed to improve NH_3 gas sensing performance including metal doping [3] and surface functionalization [4]. In this study, substrate effect by using CF_4 plasma on substrate is firstly proposed to investigate NH_3 sensing performance.

2. Experiment

The schematic of the process flow of the sensor is shown in Fig. 1. A 50 nm-thick silicon nitride (Si_3N_4) on p-type silicon was used as the substrate. Then the substrate was treated by CF_4 plasma with power at 40 W for 3, 6, and 9 min, respectively. Next, titanium (10 nm) and gold (1500 nm) layer were deposited by thermal evaporator with designed shadow mask. Graphene is formed on a copper foil by low pressure chemical vapor deposition. The graphene growth process was at 1000 °C under CH_4 and H_2 gas were introduced into the quartz tube at a flow rate of 100 and 1 sccm, respectively. The monolayer graphene were transferred from Cu foil by standard transfer method and then defined sensing area by O_2 plasma. The picture of graphene sensor is shown as in Fig 1.

3. Results and discussion

Fig. 2 shows Raman spectroscopy of graphene on the silicon nitride with different fluorination time. For the graphene on the different substrate condition, the result showed without D band and 2D/G ratio higher than 2 both confirmed the presence of monolayer graphene. Fig. 3 (a) and (b) display the comparison of the dynamic response with CF_4 plasma time measured by NH_3 and NO_2 concentration from 20 to 40 ppm and 2 to 6 ppm, respectively. The response of NH_3 and NO_2 related to concentration was shown as Fig. 4. The ammonia sensing properties is significantly improved as shown in Fig 5. Response of graphene on the Si_3N_4 with CF_4 plasma for 6 min was achieved 28.8% and 7.5% at NH_3 and NO_2 concentration of 20 ppm and 6 ppm, respectively. This improvement can be explained by the F-N dipole existed on the surface and presented the negative charge on the fluorine side to enhance graphene for ammonia adsorption as shown in Fig. 6.

4. Conclusion

In this work, an ammonia gas sensor based on fluorinated silicon nitride is fabricated to improve graphene for ammonia gas detection. In the comparison of sensor with fluorination time between 0 and 6 min, the response of NH_3 concentration at 20 ppm was increased from 21 to 28.8%. In the contrast, the response of NO_2 concentration at 2 ppm was decreased from 15.6% to 7.5%. This improvement of selectivity could be from the substrate with negative charge on the fluorine side.

References

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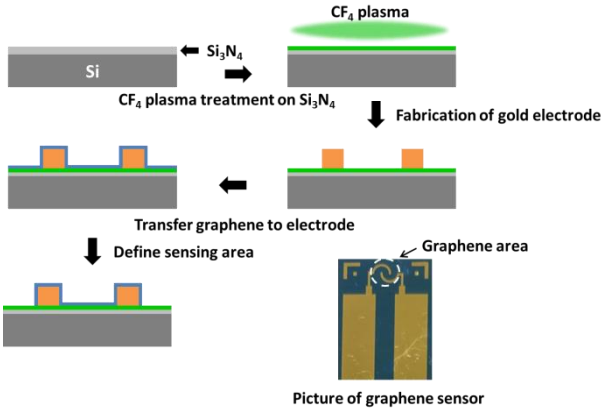

Fig. 1 Detail process flow of sensor fabrication.

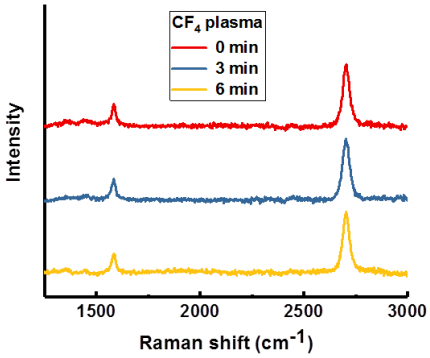

Fig. 2 Raman spectroscopy results of graphene on Si_3N_4 with different fluorination time.

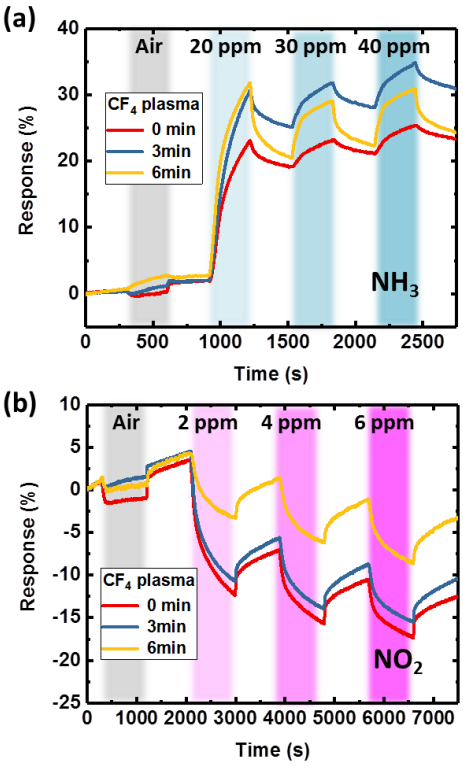

Fig. 3 Room temperature dynamic response curve of detection of (a) NH_3 and (b) NO_2 with CF_4 plasma treatment on Si_3N_4.

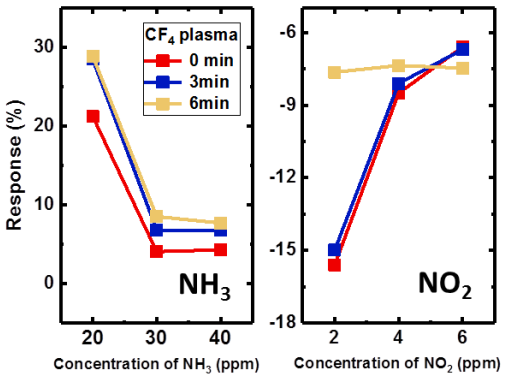

Fig. 4 The plot of response to NH_3 and NO_2 versus concentration.

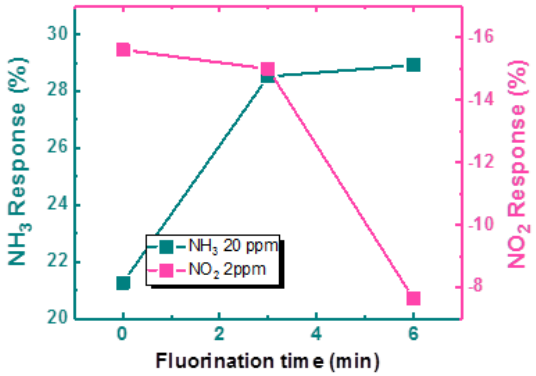

Fig. 5 The plot of response to NH_3 and NO_2 related to fluorination time.

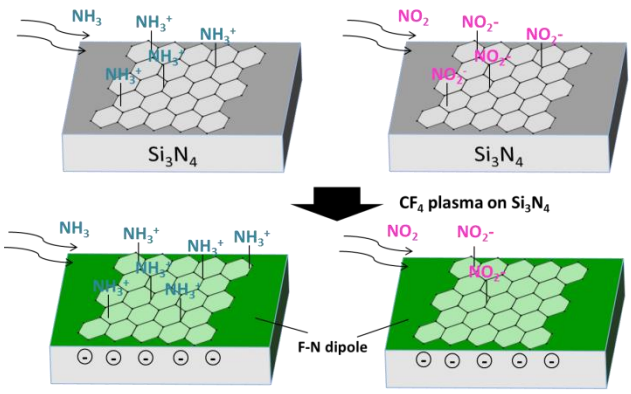

Fig. 6 The mechanism of fluorinated substrate effect on the gas adsorption.