# Improvement of ammonia sensing performance by fluorinated bilayer graphene

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## Abstract

Fluorinated bilayer graphene is treated by  $CF_4$  plasma to improve the ammonia sensing properties. Raman spectroscopy is used to investigate graphene properties after  $CF_4$  plasma treatments. Results of Raman spectral analysis in graphene with  $CF_4$  plasma show  $I_D/I_G$  ratio is increased and 2D' peak at 2954 cm<sup>-1</sup> is appeared. Gas response of fluorinated bilayer graphene is monitoring by changes in electrical resistance in difference concentration controlled by a commercial gas generator. In ammonia concentration from 15 to 100 ppm at room temperature, response of bilayer graphene with  $CF_4$  plasma treatment time of 15 min is increased 50% comparing to samples without  $CF_4$  plasma treatment.

#### 1. Introduction

Ammonia (NH<sub>3</sub>) in the human breath is an important marker for noninvasive diagnosis of liver cirrhosis.[1] Many researchers had reported the fabrication and testing of graphene gas sensors for the detection of ammonia.[2] However sensitivity and selectivity is still not good enough in real applications. Therefore some treatments were proposed to improve NH<sub>3</sub> gas sensing performance including metal doping [3] and surface functionalization. [4] In this study, a surface treatment by using indirect CF<sub>4</sub> plasma on a bilayer graphene is firstly proposed to investigate NH<sub>3</sub> sensing performance.

# 2. Experiment

The electrodes for the sensors were fabricated by the standard fabrication procedures according to our previous reports [5]. Graphene is formed on a copper foil by low pressure chemical vapor deposition. Then a CVD-grown monolayer graphene is treated by  $CF_4$  plasma and processed with power at 100 W for 15 min. Next, two fluorinated monolayer graphene were transferred from Cu foil by standard transfer method and then stacked together to be the fluorinated bilayer graphene. Detail process is shown in Fig. 1. As shown in Fig. 2, the ammonia concentration is controlled by a gas generator. A small volume of  $N_2$  gas flow is injected into permeation tube to have a well-defined gas concentration then a large volume of flow of carrier gas ( $N_2$ ) was added to dilute to the lower NH<sub>3</sub> concentration.

## 2. Results and discussion

Fig. 3 shows Raman spectroscopy of the bilayer graphene and fluorinated bilayer graphene used in this study. For the bilayer graphene, the presence of without D band and 2D/G ratio below to 2 both confirm the presence of bilayer graphene. The fluorinated bilayer graphene shows 2D' peak at 2954 cm<sup>-1</sup> and 2D/G ratio is about 0.8 which can be an evidence of the fluorinated bilayer graphene. Fig. 4(a) displays the comparison of the dynamic response with bilayer graphene and fluorinated bilayer graphene at NH<sub>3</sub> concentration of 15-120 ppm. The ammonia sensing properties is significantly improved as shown in Fig 4(b). Response of fluorinated bilayer graphene and bilayer graphene is achieved 1.18% and 0.78% at NH<sub>3</sub> concentration of 120 ppm, respectively. This improvement can be explained by the fluorinated graphene sheet with more positive charges, which can transfer of electron density to attached fluorine atoms.

## 3. Conclusion

In this work, a ammonia gas sensor based on fluorinated bilayer graphene treated by  $CF_4$  plasma is demonstrated. The results of Raman spectroscopy is used to confirm characteristics of fluorination and bilayer graphene. Fluorinated bilayer graphene is exhibited an excellent  $NH_3$  sensing performance at room temperature, which has 1.16% change of the resistance for concentration of 120 ppm.

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 $1500 \ 2000 \ 2500 \ 3000$   $CF4 \ bilayer$   $D \ G \ 2D$   $I_D/I_G=0.97$   $I_{2D}/I_G=0.8 \ 2D'$  Bilayer  $I_{2D}/I_G=1.57$   $1500 \ 2000 \ 2500 \ 3000$ Raman shift (cm<sup>-1</sup>)

Fig. 1 Detail process flow of interdigitated electrodes with the transfer of fluorinated bilayer graphene.



Fig. 2 Schematic of sensor measurement setup

Fig. 3 Raman spectroscopy results of bilayer graphene with and without  $CF_4$  plasma treatment.



Fig 4 (a) Room temperature dynamic response curve of  $NH_3$  concentration of 15, 30, 60, 90 and 120ppm with and without  $CF_4$  plasma treatment. (b) The plot of response to  $NH_3$  versus concentration.