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**Fuels of the Future**

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Room-temperature high-sensitivity detection of ammonia gas using the capacitance of carbon/silicon heterojunctions

Qingzhong Xue,*a Huijuan Chen,*a Qun Li,*a Keyou Yan,*a Flemming Besenbacher** and Mingdong Dong***

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Ammonia (NH_3) sensors based on carbon/silicon (C/Si) heterojunctions are demonstrated at room temperature (RT). Upon exposure to NH_3 molecules (0.2 ml l\(^{-1}\)) at RT, the interface capacitance of C/Si junction increases dramatically, to about 230%. The results show that C/Si junctions have high NH_3 gas sensitivity, rapid response and high recovery speed at RT. This phenomenon can be attributed to the change of the potential barrier width of the junction, which is caused by the adsorption of NH_3 gas molecules. The C/Si junctions can greatly amplify the detection sensitivity of the nano-sized carbon so that the C/Si junctions act as excellent RT gas sensors.

The search for alternative fuels has become a major national challenge. One substitute fuel that could help reduce the nation’s dependence on petroleum is anhydrous ammonia (NH_3). A variety of sensors have been extensively developed to detect ammonia gas. There has been a constant pursuit of better and new sensing materials in the past, for example, semiconducting metal oxides, conducting polymers, carbon black–polymer composites, etc.1–5 However, most of the traditional sensing materials require operation at high temperatures for enhancing the reactivity with respect to gaseous molecules. This major drawback limits traditional gas sensors for many practical applications. Recent studies show that many nanoscale materials have high sensitivity and good response speed due to their large surface areas and hollow geometry.6–10 Single-walled carbon nanotubes (SWNTs) have been demonstrated as chemical gas sensors. For example, the response time to 1% ammonia for five SWNT samples is between 1 and 2 min, and the sensitivity of (defined as the ratio between resistance after and before gas exposure) SWNTs was about 10–100.12 In addition, the effect of NH_3 on the electrical properties of the SWNT surface is also significant compared to the bulk SWNT. In fact, one-dimensional (1D) materials, including nanowires, nanorods, nanotubes, etc., usually have good gas sensitivity due to their large specific surface area, high surface binding energy, and their large surface-to-volume atomic ratio. However, it is relatively difficult to fabricate industrial gas sensors by using 1D materials. Recently, we demonstrated that the amorphous carbon film/silicon (a-C/Si) heterojunction, like individual SWNTs, have excellent NH_3 sensitivity, which is attributed to the interface effect of the (a-C/Si) heterojunctions.13

Conventional NH_3 detection is based on the conductance change when the detection surfaces are exposed to NH_3 gas.12 However, there are few reports on NH_3 detection based on capacitance changes. In this communication, we describe the deposition of amorphous carbon films on n-Si substrates using dc magnetron sputtering at room temperature (RT). It is found that NH_3 molecules have dramatic effect on the capacitance–frequency (C–f) characteristics of these a-C/Si junctions at RT. Upon exposure to NH_3 molecules (0.2 ml l\(^{-1}\)) at RT, the interface capacitance of a C/Si junction is found to dramatically increase to about 230%. The results show that these junctions have a high NH_3 gas sensitivity with high recovery speed at RT.

The carbon films were deposited on n-type Si(100) substrates using dc magnetron sputtering from a graphite target. The target was a cold-pressed graphite disk (purity >99.9%). The resistivity of the Si substrates was ca. 2–5 Ω cm. The Si substrates were pre-treated in HF solution for 5 min, followed by ultrasonic cleaning in ethanol and acetone solutions. The carbon deposition took place inside a chamber where the argon pressure was kept at 2 Pa and the Si substrates were kept at RT. The deposition power was 50 W and three deposition times (20, 40, 60 min) were used. Hall measurements of the C films indicate that these films are p-type semiconductors with very small carrier concentrations. NH_3 gas detection experiments were carried out using a simple conical flask system. The RT C–f measurements were conducted at 0.2 V using an Agilent 4284A precision LCR meter.

Broader context
Ammonia is one of the most important reactants in the chemical industry. In addition, anhydrous ammonia is also a promising non-fossil fuel. Thus, efficient detection and sensing of ammonia gas is of great relevance. Room temperature NH_3 gas sensors based on C/Si heterojunctions are demonstrated. Upon exposure to NH_3 molecules, the interface capacitance of C/Si junction increases dramatically. This capacitance sensor exhibits a fast response and a substantially high sensitivity. The C/Si junctions can be used as a new simple and cost-effective method for ammonia sensing, e.g. as room temperature sensors in the use of ammonia as a transportation fuel.
Fig. 1 shows the Raman spectra of the carbon films deposited on n-type Si surfaces for (a) 20, (b) 40 and (c) 60 min at room temperature, respectively. Two of the peaks in the Raman spectrum can be assigned as the D-band at 1350 cm$^{-1}$ and the G-band at 1580 cm$^{-1}$. The variation of the D and G peaks and the ratio of their intensities provide information on the sp$^2$/sp$^3$ ratio and the sp$^2$ cluster size in the films. As shown in Fig. 1, the Raman spectra of the films exhibit a typical characteristic of conventional diamond-like amorphous carbon: a broad peak centered at approximately 1550 cm$^{-1}$, which means there are many more sp$^3$-bonded carbon clusters in these carbon films. The surface morphologies of the carbon films have been studied by atomic force microscopy (AFM) (Fig. 2), which showed that the surfaces of the carbon films are relatively smooth. The quantitative roughness RMS values are about 0.38 nm, 0.58 nm and 0.76 nm for the 20, 40 and 60 nm films, respectively. In addition, the surface morphology and homogeneity are also important. AFM images show a 20 nm film with the best homogeneity. Fig. 3 shows the effect of NH$_3$ on the C–F characteristics of the three C/Si junctions at RT. The schematic in the inset of Fig. 3(a) illustrates the measurement setup. When the C/Si junctions are transferred from air to a 500 ml conical flask which contains 0.1 ml NH$_3$, the interface capacitances of the three C/Si junctions at 50 Hz dramatically increases to about 230, 190 and 170% for the 20, 40 and 60 min films, respectively. The surface roughness and homogeneity have a great influence on the capacitance changes, which results in the different detection sensitivities. All three surfaces have a similar roughness. In addition, the 20 nm film, which has the best capacitance increase, may also have the highest hole density. In order to further confirm the influence of NH$_3$ molecules on the capacitance of the C/Si junction, this experiment was repeated several times. Fig. 4 shows the capacitance of the C/Si junction (20 min) response to air and NH$_3$ at given frequencies of (a) 50, (b) 1000, (c) 10000, and (d) 100 000 Hz, respectively. It can be seen, when the junction is transferred form air to a 500 ml conical flask which contains 0.1 ml NH$_3$, the initial capacitance of the junction at 50 Hz increases rapidly to about 230% and the sensitivity decreases with increasing frequency. Moreover, the capacitance of the junction can be also recovered rapidly when the junction is transferred from NH$_3$ to air for 30 s (as shown in Fig. 5). The results show that C/Si junctions have an immediate response, high sensitivity and good reproducibility for NH$_3$ gas detection. C/Si junctions can be also used as other gas sensors e.g. for ethanol detection. The NH$_3$ sensitivity of the C/Si junctions can be further understood by the adsorption process of the carbon films and the change of the contact potential barrier of the junction. The contact capacitance ($C_T$) of an abrupt junction can be calculated from equation (1).$^{14}$

$$C_T = A \sqrt{ \frac{\varepsilon_1 \varepsilon_2 q N_A N_D}{2(N_D + N_A)(V_D - V)}}$$  (1)

where $q = 1.602 \times 10^{-19}$ C, $A$ is the interface area, $N_A$ is the hole density of the carbon film, $N_D$ is the electron density of the silicon, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants of the carbon film and n-Si, respectively, $V_D$ is the contact potential barrier of the abrupt junction, and $V$ is the applied voltage.

It has been reported that NH$_3$ molecules can be considered as electron donors, which can donate electrons to carbon nanomaterials during the adsorption progress.$^{15,16}$ When the C/Si junction is exposed to NH$_3$ molecules, NH$_3$ molecules will interact with the carbon film by replacing pre-adsorbed gas molecules due to the different adsorption energies of the molecules (NH$_3$, O$_2$, N$_2$, CO$_2$) interacting with the carbon film.$^{14}$ For NH$_3$ gas, some electrons from NH$_3$ molecules are donated to the carbon film so that the Fermi level of the...
carbon film will be enhanced. Therefore, the difference between the Fermi levels of the carbon film and Si will decrease after NH$_3$ adsorption. The carrier diffusion at the surface of the C/Si junction will decrease and the width and value of the contact potential barrier will decrease after the carbon film is exposed to NH$_3$ gas. According to eqn (1), the contact capacitance of the C/Si junction will increase with the decrease of contact potential barrier. Hence the corresponding contact potential barrier change of these C/Si junctions, caused by the NH$_3$ adsorption, can greatly amplify the NH$_3$ detection sensitivity of the carbon film itself so that the C/Si junctions can act as excellent gas sensors at RT. In contrast, when the C/Si junctions were exposed to air again, NH$_3$ gas molecules were desorbed from the carbon film resulting in the electrons being released from the carbon film, so that the original $C$-$f$ characteristics of the junction were recovered.

Conclusions

For ammonia to be widely used as a fuel, one of the major concerns is inhalation hazards. These simple and cost effective C/Si junctions can greatly amplify the sensitivity of ammonia detection. In addition, NH$_3$ gas detection based on C/Si heterojunctions is performed at RT, which will enable the technique to be used for future practical applications. Upon exposure of the interface of a C/Si junction to NH$_3$ (0.2 ml l$^{-1}$), the capacity is found to dramatically increase to about 230%. The results show that the C/Si junctions have high NH$_3$ gas sensitivity, rapid response and recovery speed at RT. These phenomena can be attributed to the change of the potential barrier width of the C/Si junction after NH$_3$ gas molecule adsorption. Therefore the C/Si junctions can greatly amplify the sensitivity of the
nano-sized carbon with simplicity and low cost. The C/Si junctions could also act as excellent RT gas sensors for the use of ammonia as transportation fuel.

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