GaN nanowires decorated with Pd for methane gas sensor

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Abstract. In this study, palladium (Pd)-decorated gallium nitride (GaN) nanowire have been prepared for room-temperature methane (CH\textsubscript{4}) gas sensors. The material was fabricated via MOCVD method combined with subsequent magnetron sputtering process and characterized by SEM technique. The SEM images indicate that the presence of different thickness of Pd film on the surface of the nanowires. When used for methane gas sensing, with the assistance of UV light, the 10nm Pd-decorated GaN nanowire sensor has the highest response to 200ppm methane, which were about 2 times higher than that of pure GaN samples. What’s more, 10nm Pd-decorated GaN sensor also has the lowest detection limit (20ppm) and the shortest response time (<10s). Thus, the application of Pd-GaN nanowire as methane gas sensor will have board prospects.

1. Introduction

Methane (CH\textsubscript{4}) is the hydrocarbon with the lowest carbon content and the simplest organic matter in nature, it is also the main constituent of natural gas. As a reliable and efficient energy source, methane has been widely used for industrial and domestic application. However, it is extremely flammable and easy to cause an explosion which can bring great damage and serious casualties in air at concentrations between lower explosion limit (LEL) of 4.9\% and an upper explosion limit (UEL) of 15.4\% [1]. Methane is colorless, odorless and non-toxic [2] so it is difficult to detect via traditional methods. Hence, develop a reliable and highly sensitive sensors for methane detection at low concentration to prevent accidental explosions and ensure the safety of life is imperative.

In present, the CH\textsubscript{4} sensors including infra-red adsorption spectroscopy sensors, electrochemical sensor, and semiconductor gas sensors, etc [3–7]. In recent years, some semiconductor materials such as SnO\textsubscript{2} [8-10], ZnO [11, 12], TiO\textsubscript{2} [13, 14], In\textsubscript{2}O\textsubscript{3} [15, 16], WO\textsubscript{3} [17, 18], etc, have been widely used to detect the dangerous and harmful gas. Semiconductor gas sensors are the most widely used because of their excellent features: high response, good electrical, optical behavior, easily integrated and low price. Compared with above-mentioned materials, the GaN have the following advantages: (1) working at the room-temperature leads to low power consumption; (2) high electron mobility, good chemical stability; and (3) decreasing the resistance by several orders of magnitudes.

This study is the first report of GaN nanowires used for methane gas sensing. Because of the sensing performance can be improved by loading a small amount of noble metal and Pd is the most active noble metal for CH\textsubscript{4} oxidation\textsuperscript{19}, we optimize our GaN nanowire gas sensor by decorating different thickness of Pd. The CH\textsubscript{4} gas-sensing properties were investigated. The obtained Pd-GaN nanowires gas sensor showed high sensitivity (detection limit lower than 20ppm), short response time (<10s) and high stability at room-temperature. Furthermore, the sensing mechanism was discussed.
2. GaN nanowire fabrication and testing

In our previous work \cite{20}, the characterization of direct-bridge growth of aligned GaN nanowires over the trench of GaN-coated sapphire substrate was performed. The GaN nanowires showed great performance in NO\textsubscript{2} sensing. On this basis, we optimize the properties of the sensor, and applied it in CH\textsubscript{4} sensing. We used magnetron sputtering method to decorate Pd onto the surface of nanowires. The sputtering speed is 0.5Å/s. On the same sample, the resistance of 0/2/6/10nm Pd-decorated nanowires is 104.3 Ω/103.02 Ω/102.68 Ω/101.98 Ω, respectively. The decrease in resistance due to Pd enhances surface conductivity. This change of resistance also confirms that there is no formation of continuous Pd film at the bottom of the trench. In order to investigate the morphology of the prepared samples, scanning electron microscope analysis was performed. The SEM images of the trench of samples are shown in Figure 1.

Figure 2(a)-(d) show the single nanowire micrographs with different thickness Pd decorated respectively. As it is clearly seen in SEM images, Pd had obvious agglomeration instead of forming metal film. As the Pd’s thickness increased, the agglomerated particles distributed into regular shapes and the average size of nanoparticles grew bigger. This distribution facilities the UV light isn’t completely blocked out in subsequent testing. The above analysis confirms the successful assembly of Pd-decorated GaN nanowires.

![Fig.1 SEM images of the trench of samples (a) top view, (b) cross-sectional view.](image-url)
Fig. 2 SEM images of the bridging NWs with different thickness of Pd decorated (a) 0nm, (b) 2nm, (c) 6nm and (d) 10nm.

We detect methane gas in confined space. The change of resistance of sensors are calculated by bridge circuit. The gas response was defined as \((R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}\), where \(R_{\text{gas}}\) and \(R_{\text{air}}\) are the nanowires resistances in CH₄ and air, respectively.

3. Results and Discussion
As shown in Figure 3(a,1), the responses of pure GaN nanowires to various CH₄ concentrations (0–500ppm) were measured at room temperature. When exposed to CH₄ gas under 1400\(\mu\)W/cm² power UV light, the resistance first decrease and then reaches a stable value. The minimum detection limit is 100ppm.
Fig. 3 (a) The gas responses of GaN nanowires with different Pd decorated to various CH$_4$ concentrations (0-500ppm). (b) The gas response of 10nm Pd-decorated nanowires to CH$_4$ under different intensity (0-1400μW/cm$^2$) of UV light.

The response of Pd-decorated GaN nanowires is shown in Figure 3(a,2−4). The response magnitude and response/recovery speed increased after the sensor was decorated by Pd. The detection limit reduced to 20ppm when the thickness of Pd is 10nm (The detection is indicated by the red arrow in the figure). The response time at 20ppm as low as 10s. The gas sensing result is plotted in Figure 4(a). The gas response magnitude of 10nm-Pd decorated GaN is 2 times higher than pure GaN.

The gas response of 10nm Pd-decorated GaN nanowires under different intensity of UV light is shown in Figure 3(b). In the dark, the detection limit is 500ppm. The response can be improved by using UV illumination. The detect limit was increased 25 times when the UV power is 1400μW/cm$^2$. The photoelectric response and response time are shown in Figure 4(b). Because of the Pd on the surface blocked the UV light, the photoelectric response magnitude and response speed decrease as the thickness of Pd increase. However, the gas response still increase when UV power increases beyond 1400μW/cm$^2$.

Cycle measurements of 200 ppm CH$_4$ were shown in Figure 5. It is clear that the sensor has good repeatability. The response magnitude increases more than 2 times as Pd’s thickness increases from 0 to 10 nm. It’s response/recover time are plotted in Figure 4(c). The response time reduced remarkably from 80 to 25s.
Fig. 4 (a) The line chart of gas sensing result (b) Photoelectric response and response time of the sensors, (c) The gas response/recover time of 10nm Pd-decorated nanowires to 200ppm CH₄.
The detection of CH$_4$ sensor is based on the resistivity change of the materials. The resistance of the sensors decreased upon exposure to CH$_4$, while the resistance recovered to its initial value when CH$_4$ was replaced by air. This experimental phenomenon indicated that the GaN nanowire had the n-type semiconductor behavior. The surface of the GaN nanowires provides many active sites for oxygen’s adsorption and desorption. When the sensors are exposed to air atmosphere, the oxygen molecules absorbed on the nanowires’ surface obtain the electrons from the conduction band and eventually form oxygen ions (O$^-$, O$_2^-$ and O$_{2^-}$). These adsorbed oxygen molecules lead to the formation of electron depletion layer. Due to electrons are the main carriers of n-type semiconductor, the resistance of the sensor increases \[20\]. When CH$_4$ gas exist in the air, CH$_4$ molecules react with the oxygen ions on the surface of GaN nanowires. This oxidation-reduction reactions release the electrons back to the conduction band so the thickness of the electron depletion layer and the resistance of the sensor decreases.

The CH$_4$ sensing performance was improved after the Pd was decorated on the surface of the nanowires. The possible optimization mechanism is mainly attributed to the following two aspects. For one thing, Pd has powerful spillover effect which can catalyze the dissociation of methane and oxygen molecules \[21\]. At the surface of the Pd-decorated GaN nanowires, the oxygen molecules dissociate to oxygen atoms so they are more easily to obtain electrons from the conduction band. Thus, the adsorption quantity of oxygen and the molecule-ion conversion rate increase. When in CH$_4$ atmosphere, Pd atom promote the dissociation of C-H bond to form CH$_3$ and H, lower the activation energy of oxidation-reduction reaction. For another thing, the work function of GaN is lower than Pd so when Pd is contact with GaN nanowire, the band near the interface bends upward and form Schottky barrier. The electrons transfer from GaN to Pd so that there would be a depletion layer beneath the GaN surface. The absorbed oxygen increases the barrier height and the width of depletion layer. In opposite, the barrier height and the width of depletion layer decrease when CH$_4$ react with the absorbed oxygen and then release the electron back to the conduction band. The related band diagram is shown in Figure 6. The corresponding reaction processes are described by following Eqs.(1)–(2) \[22,23\]:

\[
\text{CH}_4 \xrightarrow{\text{Pd}} \text{CH}_3 + \text{H} \tag{1}
\]

\[
\text{CH}_3 + 4\text{H} + 4\text{O}^- \xrightarrow{\text{Pd}} \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \tag{2}
\]

Fig.5 Cycle measurement of GaN nanowires with different thickness of Pd decorated to 200ppm CH$_4$
When the sensor is under UV illumination, the photons are absorbed and excite electron-hole pairs. Due to the carrier concentration increases, these photon-generated carriers speed up the rate of oxidation-reduction reaction. The basic reaction process is similar to the process in the dark, but its magnitude is increased.

![Fig. 6](image)

**Fig. 6** The band diagram of sensing mechanism (a) pure GaN, (b) Pd-decorated GaN.

4. Conclusion
In this paper, a methane gas sensor based on Pd-decorated GaN nanowires is first proposed, fabricated and tested. The Pd metal forms uniform particles on the surface of GaN nanowires. Compared with pure gas sensors, the introduction of Pd decoration significantly improve the performance of the sensor. With the assistance of UV light, the 10nm Pd-decorated GaN nanowires gas sensor has the lowest detection limit (20ppm) at room-temperature. Moreover, it shows fast response speed and good repeatability.

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