UV irradiation-assisted ethanol detection operated by the gas sensor based on ZnO nanowires/optical fiber hybrid structure

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Abstract: In this work, the gas sensor based on a novel ZnO nanowires/optical fiber hybrid structure was proposed in order to enhance the sensing properties of ethanol detection with UV irradiation. The results showed that UV irradiation was able to enhance the sensitivity and shorten the response time, and the sensor performed a good long-term stability as well. The UV-assisted sensor could response to the low concentration at ppb-level of ethanol at relatively lower temperatures, and a sensing mechanism was proposed to understand the effect of UV irradiation in the ethanol detection process. The gas sensor based on the ZnO nanowires/optical fiber hybrid structure is practical for detecting gas with ultra-low concentration and the combination of UV irradiation is an effective approach to develop high-performance gas sensors.

Keyword:

UV irradiation

ZnO nanowires

Optical fiber

Gas sensor

1. Introduction

One-dimensional Zinc oxide (ZnO), as a kind of II-VI semiconductor with the wide band gap of 3.37 eV, has been widely studied for nanotechnology [1,2]. It has potential applications in gas sensing due to its low cost, non-toxicity, high electron mobility and thermal stability under the operating temperature. In the past years, a variety of ZnO nanowire-based devices have been developed for gas sensing, such as ethanol sensor [3-7], oxygen sensor [8,9], VOC sensor [10], triethylamine sensor [11], and multifunctional sensor [12]. The underlying sensing mechanism has also been investigated [13,14]. ZnO nanowires are studied for gas sensing because of the large surface area of gas adsorption and the anisotropy properties that exhibit extreme different surface energy. The dominant high-oriented polar (002) plane in ZnO crystal is highly reactive and electrostatically unstable. It is composed of Zn-terminated (0001) plane and O-terminated (000-1) surface, where the positive polar (0001) plane plays an important role in increasing radical species adsorption on the surface [15-17].

For better sensitivity towards lower concentration of the target gas at lower temperature, several techniques have been used to develop ultra-sensitive gas sensor, such as the incorporation of transition-metal oxides and the combination with UV irradiation. UV irradiation has been demonstrated as an efficient attempt to achieve high sensitivity at low temperatures for gas sensors with different morphologies of metal oxides, such as nanoparticles [18,19], films [20,21], nanowires [22,23], nanorods [24], fibers [25]. The effects of surface properties and morphologies to the sensitivity have also been investigated [26]. B. Costello et al. utilized ZnO to detect volatile organic compounds under UV-LEDs and found that the illumination could promote the catalytic oxidation reaction between the reducing gases and the oxygen ions [27]. S.-W. Fan et al. used a UV light to enhance the sensitivity and the response/recovery rate of ZnO nanostructures to ppm-level for the H₂ detection. It was found that the electrons produced by UV light promote the adsorption of oxygen [28]. Y.-H. Ho et al. fabricated the ZnO nanostructures with high surface-area and achieved room-temperature VOC sensing under UV light activation. The sensitivity was 4.18 times higher than that of the ZnO nanostructures in the absence of UV light activation

[29]. J. Cui et al. synthesized the ZnO nanofibers as UV photoelectrical sensor, which exhibited high response, rapid response/recovery speed and an outstanding selectivity to HCHO when irradiated with a 365 nm UV-light at the room temperature [30]. S.T. Tan et al. synthesized ZnO nanorod array for the room temperature photoluminescence-based CO gas sensing. These ZnO nanorods were excited by a continuous wavelength Argon ion deep UV laser (244nm) and were able to detect CO gas with the concentration as low as 10 ppm within 2.5 min [31]. Y. Chen et al. synthesized hollow ZnO microspheres with the carbon-template assisted method, the chemiresistive gas sensor based on hollow ZnO microsphere showed an excellent sensitivity, fast response and excellent selectivity to ethanol with the activation of low-powered UV-led [32]. The above reported results indicate that UV irradiation is a promising technique to improve the sensing properties of ZnO nanostructures. However, the existing studies about UV-assisted gas detection usually adopt external irradiation over the sensing structures with UV laser or UV lamp. The gas sensor was bulky, and the energy of UV light was dissipated due to scattering, which was not suitable to the practical applications.

In this study, we developed a novel gas sensor based on a hybrid structure, which integrates ZnO nanowires on the optical fiber surface. The structure was fabricated by seed-layer sputtering on the fiber surface followed by hydrothermal synthesis. The approach has the advantages of simplicity, low-cost, high-yield with uniformity of ZnO nanowires on the fiber surface comparing with other methods such as patterned growth, surface-induced growth and self-assembly [2,33]. The design was also efficient in utilizing the UV light through irradiation from the inside of the optical fiber. The properties of the gas sensor were studied afterwards, showing that the gas sensor with UV irradiation indicated excellent sensitivity to different concentrations of ethanol, even at relatively lower temperature.

2. Experimental

Synthesis of the hybrid structure

The ZnO nanowires/optical fiber hybrid structure was synthesized by a two-step

process. In the first step, the cladding was stripped away from the optical fiber by acetone to expose the core as the growth substrate, the cladding was stripped away from the optical fiber by acetone to expose the core as the growth substrate, and a seed layer of ZnO film was deposited on the outer wall surface of the fiber core by magnetron sputtering. The thickness of the seed layer was around 50 nm, which was controlled by the sputtering rate of 10 nm/min for 5 minutes in this work. The sputtering rate was estimated from the measurement of ZnO film thickness on planar glass substrate under a defined sputtering time, and the planar film thickness could be easily measured by the profilometer. The core diameter of the multimode optical fiber is 200 μm , and the ZnO target utilized in this work possessed a purity of 99.95%. Then, the upper facet of the fiber was connected with the UV laser source, and the lower end of the fiber with exposed core was immersed into the growth solution, which contained zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMT) mixed in deionized water. By adjusting the growth duration, temperature and the solution concentration, the growth density of ZnO nanowires could be controlled on the outer wall surface of the fiber by the typical hydrothermal process [2]. The growth process was operated in the mixed solution with the ratio of 2:1 for $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ and HMT and at the temperature of 90°C for 3 hours. Fig. 1 shows the schematic of the ZnO nanowires/optical fiber hybrid structure. In this study, 8 gas sensors were fabricated with the ZnO nanowires/optical fiber hybrid structure to investigate UV irradiation-assisted sensing performance for ethanol.

Fig. 1. Schematic of the ZnO nanowires/optical fiber hybrid structure.

Characterization

The microstructural properties of the ZnO nanowires were characterized by field scanning electronic microscopy (SEM, FEI Nova NanoSEM 450) and transmission electron microscopy (TEM, FEI Tecnai G2 S-TWIN). The crystallography phase and purity of the ZnO nanowires were characterized by X-ray diffract meter (XRD, X'Pert PRO) with radiation from a Cu target ($K\alpha$, $\lambda = 0.15418$ nm).

Gas sensing measurement

The gas sensing properties were measured with a static test system, including a UV laser source, a gas chamber and a resistance measurement system.

The monochromatic UV light was provided by the UV laser source. The gas sensor based on the ZnO nanowires/optical fiber hybrid structure was connected to the UV laser source, with the propagating in the fiber along the axial direction from the input end. The UV laser source is a single-wavelength fiber coupling semiconductor lasers. The laser system is a continuous-wave system. The wavelength of UV light is 365 nm. The regulating range of the power is from 0 to 130 mW.

The ethanol gas was prepared with thermal evaporation and scalable dilutions. Based on the known volume of a gas tank and gas concentration calculation, the ethanol gas with the highest concentration of 1000 ppm was firstly prepared in the gas tank by thermal evaporation with analytical grade ethyl alcohol in Ar, where the water

content of Ar is 0.5 ppm. Then part amount of ethanol gas with 1000 ppm was injected into the gas chamber with the known volume of 20 L to dilute to the designed concentration for testing. The injected amount was determined based on the final concentration of the diluted gas in the gas chamber. The diluted ethanol gas used in the experiment was prepared with the concentration of 50, 100, 150, 200, 300, 400, and 500 ppb, respectively.

Fig. 2 (a) shows the schematic of the gas sensor, and Fig. 2(b) illustrates the light transmission in fiber of the hybrid structure. The resistance of the gas sensor was measured by a commercial Chemical Gas Sensor-8 Intelligent Gas Sensing Analysis System (ELITE TECH), where DC was used. Two measuring ends of the gas sensor were respectively bonded to the commercial Ag-Pd electrode with the width of 0.5 mm by conductive silver adhesives, and then connected to the testing circuit of the system to measure the real-time resistance of the gas sensor.

Fig. 2. (a) Schematic of the gas sensor; (b) vertical section of the gas sensor.

This study will focus on investigating the effects of UV irradiation on the gas sensing performance of the ZnO nanowires/optical fiber hybrid structure, where conducting electrons can be generated with the adsorption of energy from ultraviolet photons. Before initial test, the sample was aged under the working voltage to ensure its stability of the resistance after the first UV irradiation in the experiment. For the successive testing, the gas sensor would be sat in the ventilated hood for one day to desorb ethanol sufficiently after each test, and the resistance of the sensor would be checked to ensure recovering to the initial value. In this study, each gas sensor was

repeatedly tested for 10 times to ensure reliable results.

The measurement system also provides the simultaneous heating function to the gas sensor under the heating mode. The working temperature could be controlled through the heating current with the heating element of Ni-Cr alloy. The tests were operated at the temperatures of 150, 200, 250 and 300°C respectively. The relative humidity in the gas chamber was 75%, which was controlled by employing saturated salt solution of sodium chloride.

R_a and R_g are the resistances of the gas sensor in air and in the analyte respectively. The response of the sensor is defined as the ratio of R_a to R_g . The time taken by the resistance to change from R_a to $R_a - 0.9 \cdot (R_a - R_g)$ is defined as the response time when the sensor is exposed to the analyte. The time taken by the resistance to change from R_g to $R_g + 0.9 \cdot (R_a - R_g)$ is defined as the recovery time when the sensor is retrieved from the analyte.

3. Results and discussion

Fig. 3(a) shows the SEM images of the cross section of the obtained ZnO nanowires/optical fiber hybrid structure. The densely packed ZnO nanowires on the outer wall surface of the fiber were synthesized by the hydrothermal method. The SEM image of the ZnO nanowires is presented in Fig. 3(b). The length of the ZnO nanowires was about 1.2 μm and the diameter was about 100 nm.

Fig. 3. (a) the cross section of the obtained ZnO nanowires/optical fiber hybrid structure; (b) SEM image of the ZnO nanowires.

Fig. 4 shows the results of XRD analysis for the ZnO nanowires on the outer wall surface of the multimode optical fiber. It was found that all peaks were indexed

to a hexagonal wurtzite ZnO structure with the datasheet by the JCPDS card no. 36-1451. No other impurity peaks, such as complex zinc, were found in the diffraction spectra. A dominant (002) peak that located at $2\theta = 34.4^\circ$ was observed, indicating that the ZnO nanowires preferred to grow along the c-axis orientation. Fig. 5 shows the TEM images of the ZnO nanowires, where a continuous lattice fringe was observed, confirming that the ZnO nanowires were formed on the outer wall surface of the fiber. The adjacent atomic lattice distance was 0.26 nm, which verified that the favourable growth orientation of the ZnO nanowires were on the (002) orientation.

Fig. 4. XRD analysis for the ZnO nanowires.

Fig. 5. TEM images of the ZnO nanowires.

Fig. 6 shows the resistance of the ZnO nanowires/optical fiber hybrid structure

under the first and successive UV irradiation of 120 mW in the air at 300°C. It shows that the initial resistance was around 1.02 MΩ without UV irradiation, and the resistance decreased under UV irradiation. For the first time of UV irradiation, it took 272 s for the resistance to decrease from 1.02 to 0.51 MΩ, and 3980 s was needed to recover to the resistance of 0.98 MΩ when UV irradiation was stopped. For the successive testing, the resistance was repeatedly varied at 0.51 and 0.98 MΩ with and without UV irradiation. It suggests that UV irradiation improves that conductivity of the ZnO nanowires/optical fiber structure, which is due to valence electrons of the ZnO nanowires jumped into conduction band with the good absorption of the energy from ultraviolet photons.

Fig. 6. Resistance of the ZnO nanowires/optical fiber hybrid structure under the first and successive UV irradiations of 120 mW in the air at 300°C.

Fig. 7 further shows the resistance of the ZnO nanowires/optical fiber hybrid structure in the air at 300°C under UV irradiation with the power of 30, 60, 90 and 120 mW respectively. With the increase of the power, the resistance decreased, and then recovered to 0.98 MΩ after UV irradiations. From Fig. 6 and Fig.7, it has been demonstrated that the resistance of the sample structure is reversible after the first UV irradiation of 120 mW when the irradiation power is controlled no more than 120 mW. In this study, The UV irradiation power was controlled to be no more than 120 mW, and each gas sensor was treated with UV irradiation to exclude the effect of the first UV irradiation, which was critical for the sensor fabrication. The change of the

resistance caused by the power was due to the energy deposited from UV irradiation, and the resistance remained stable when the adsorption of the energy was saturated after a period of time.

Fig. 7. The resistance of the ZnO nanowires/optical fiber hybrid structure in the air at 300°C under UV irradiation with the power of 30, 60, 90, and 120 mW, respectively.

Fig. 8 shows the measurement results of dynamic response of the gas sensor to different concentrations of ethanol at 300°C, where Fig. 8(a) and (b) show the results measured without and with UV irradiation of 120 mW, respectively. The response of the gas sensor could be obtained by calculating these measured results of dynamic response, which is shown in Fig.9. The detection concentrations of ethanol were 50, 100, 150, 200, 300, 400, and 500 ppb, respectively. The response increased with the increase of concentration, and the response under UV irradiation was much higher than that without UV irradiation.

Fig. 8. The dynamic response to different concentrations of ethanol at 300°C (a) without UV irradiation and (b) with UV irradiation of 120 mW.

Fig. 9. Transient response of the gas sensor to different concentrations of ethanol at 300°C.

Fig. 10 shows the response time of the gas sensor towards ethanol at 300°C. The response time of two gas sensor was almost the same with the concentrations of 50 ppb and 100 ppb. The response time of the gas sensor with UV irradiation was shorter than that without UV irradiation with the concentration of 150, 200, 300, 400 and 500 ppb respectively. It confirmed that UV irradiation contributed to shorten the response time of the gas sensors.

Fig. 10. Response time of the gas sensor towards ethanol at 300°C.

Fig. 11 shows the long-term stability of the gas sensor with UV irradiation of 120 mW. The resistance of the gas sensor was measured every two days towards different concentrations of ethanol at 300°C. The response was stabilized and the gas sensor with UV irradiation performed good long-term stability.

Fig. 11. Long-term stability of the gas sensor with UV irradiation of 120 mW.

Fig. 12 shows the response of the gas sensor to low concentrations of ethanol with 50, 100, 150, 200, 300, 400 and 500 ppb at different temperatures. The gas sensor could response to ethanol with the concentration of 50 ppb at the working temperature of 300°C, as shown in Fig. 12(a). In general, the response of the gas sensor to ethanol reduced as the temperature decreased, as shown in Fig. 12 (b), (c) and (d). The gas sensor with UV irradiation of 120 mW responded to 150 ppb of ethanol at 250°C, and 200 ppb of ethanol at 200°C, while the gas sensor without UV irradiation returned no response under the same condition. The gas sensor with UV irradiation of 120 mW still responded to the concentration of 300 ppb at the temperature as low as 150°C, and the gas sensor without UV irradiation didn't work at 150°C.

Fig. 12. Response of the gas sensor to different concentrations of ethanol at (a) 300°C, (b) 250°C, (c) 200°C and (d) 150°C.

The working mechanism of the gas sensor relies on the surface reactions such as oxidation or reduction caused by different gas exposures [34]. When the gas sensor is exposed to the air, the oxygen molecules are adsorbed on the surface. The adsorbed oxygen molecules combine electrons from the conduction band and the electron depletion region extends from the surface [35]. This progress can be described by following equations:

As shown in Fig. 6, it took 272 s for the resistance to decrease from 1.02 to 0.51 MΩ with UV irradiation due to the slow adsorption process of oxygen molecules on the ZnO surface. When the UV was switched off, the resistance would recover from 0.51 to 0.98 MΩ with 3980 s. The slow recovery may be attributed to the very slow process of the oxygen molecules desorption. In this experiment, when ethanol is introduced at moderate temperature, the reaction between the adsorbed oxygen and ethanol molecules on the semiconductor material surface can be depicted as follows:

It can be seen from the above reactions that some of the chemisorbed oxygen ions in the form of O^- and O^{2-} are removed for oxidizing ethanol, and release electrons back to the conduction band, leading to the increase of the conductivity [36].

To further understand the sensing mechanism of UV irradiation-assisted detection of ethanol, the schematic is also proposed in Fig. 13. The band gap of ZnO is 3.2 eV on glass substrate which is lower than the photon energy of UV irradiation with 3.4 eV [37-40], therefore the ultraviolet photons could be absorbed by the ZnO nanowires under inner irradiation from the glass fiber with the ZnO nanowires/optical fiber hybrid structure. Therefore the UV absorption would produce more conducting electrons and improve the conductivity of the structure. The increment of conducting electrons under UV irradiation promotes the reactions as shown in Eq. (1) and (2), which is also illustrated by Fig. 13 (a) and (b). Fig. 13 (c) and (d) further illustrate the response mechanism of ethanol molecules on the ZnO nanowires, where UV irradiation offered more oxidation of ethanol as shown in Eq. (3) and (4). Therefore, the gas sensor with UV irradiation had higher sensitivity and less response time than the gas sensor without UV irradiation.

Fig. 13 Schematic of oxygen absorption in adjacent regions of ZnO nanowires (a) without UV irradiation and (b) With UV irradiation. Schematic of ZnO nanowires response to ethanol (c) without UV irradiation and (d) With UV irradiation.

Comparing with the literature reports [17-27,29,32], the sensor structure presented in this work is unique, where the fiber is as the core and the ZnO nanowire array is as the shell. This unique structure can irradiate UV light from the inner core to the outside shell. The enhancement of sensitivity of the structure on ethanol detection reaches ppb-level, while those literature reports were still in ppm-level. It suggests the hybrid core-shell structure with inner UV irradiation is advantageous for application in ultra low concentration detection of ethanol, and the structure design strategy may be also applicable to sense many other low-concentration gases.

4. Conclusions

A novel gas sensor was developed based on the hybrid structure obtained by ZnO nanowires grown over the optical fiber surface. It was a sensor integrated the sensitive element with UV irradiation system. The UV light propagated in the fiber from one end along the axial direction when the gas sensor was working. The results showed that the sensitivity and the response time of the gas sensor were greatly improved due

to UV irradiation. The gas sensor with UV irradiation could respond to ppb-level concentration of ethanol at relatively lower temperature. It suggests that the conducting electrons in the ZnO nanowires generated by UV irradiation promote the reduction of ethanol, leading to higher sensitivity and less response time. The novel gas sensor based on the ZnO nanowires/optical fiber hybrid structure was a good candidate for gas detection in practice.

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