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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.

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 (0 0 2) plane in ZnO crystal is highly reactive and electrostatically unstable. It is composed of Zn-terminated (0 0 0 1) plane and O-terminated (0 0 0 −1) surface, where the positive polar (0 0 0 1) 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 H_2 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 (244 nm) 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

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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

2.1. 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 min 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 ($ZnNO_3{\cdot}6H_2O$) 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 $ZnNO_3{\cdot}6H_2O$ and HMT and at the temperature of 90 °C for 3 h. 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.

2.2. 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 (Kα, λ = 0.15418 nm).

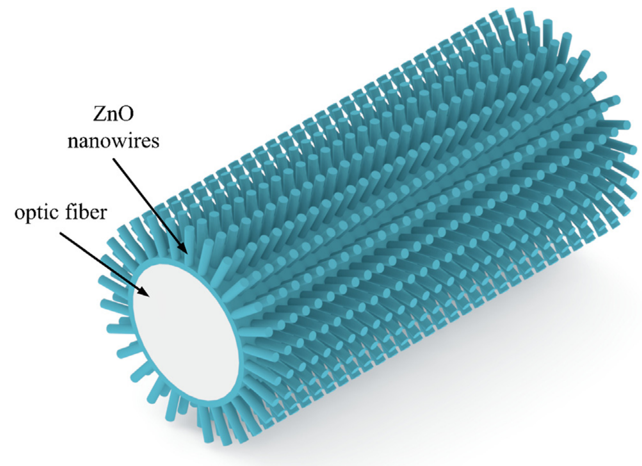

Fig. 1. Schematic of the ZnO nanowires/optical fiber hybrid structure.

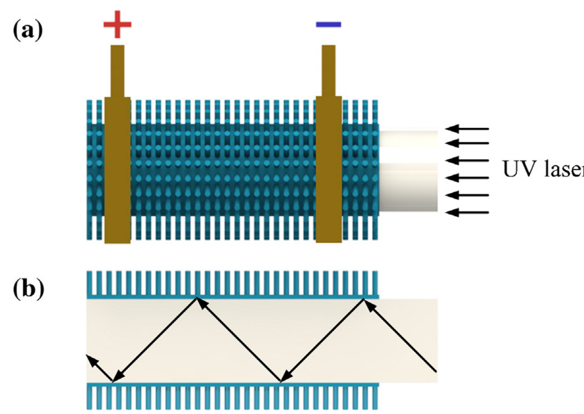

Fig. 2. (a) Schematic of the gas sensor; (b) vertical section of the gas sensor.

2.3. 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