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Enhancing the performance of room temperature ZnO microwire gas sensor through a combined technology of surface etching and UV illumination

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ABSTRACT

Enhancing the performance of individual micro/nanowires based room temperature gas sensors is a big challenge for real-time detection of toxic gases. In this work, we developed a surface etching method to increase the sensitivity of individual ZnO microwire (MW) based gas sensor. The etching of the MW increases the adsorption sites for gas molecules on it by increasing the specific surface area and the surface density of single ionized oxygen vacancies. This leads to a ~20-fold increase of the gas sensor's sensitivity. When working under 148.8 μW cm^{-2} of UV light, the sensitivity is further increased to 411%. Meanwhile, the response and the recovery time decreases to ~20% and ~2% of the values in dark condition, respectively. As a result, the individual ZnO microwire based gas sensor's performance was greatly enhanced, and it has great potential to be used as a room temperature gas sensor towards NO_2.

1. Introduction

Detecting toxic environmental pollutants such as NO_2 in real-time at room temperature is very important to avoid their damages to the health of plants, human beings, and animals [1]. Consequently, gas sensors incorporated into portable systems such as wearable devices and hand hold terminals are attracting considerable interests [2]. These systems require both small device size and low power consumption. Recently, gas sensors fabricated with individual micro/nanowires, which meet the pressing demands, are studied [3]. However, seldom works focused on improving the sensitivity of these gas sensors, which has limited the development of real-time detection of toxic gases [4].

To improve the gas sensors' sensitivity, adequate amount of adsorption sites for gas molecules are demanded for the sensing materials [5]. Under this principle, semiconducting nanomaterials with large specific surface area are widely used in gas sensors' fabrication [6]. In previous reports, micro/nanowires with large specific surface area are synthesized by increasing their porosity [7,8]. However, their polycrystal nature makes them having low conductivity, and limits their application range. Herein, we demonstrate a surface etching method to increase the specific surface area of ZnO microwires (MWs). The sensitivity of the gas sensor fabricated with the etched ZnO MW is largely enhanced compared with that of the original one. Furthermore, the gas sensor is successfully used to detect NO_2 at room temperature, under continuous UV illumination.

2. Experiments

ZnO MWs were synthesized using chemical vapor deposition (see Supporting information). Each ZnO MW was attached onto a pre-cleaned glass substrate by carbon paste. MWs with same size were etched with HCl water vapor for 0, 5, 10, 15, and 20 s, respectively. Each gas sensor was fabricated by depositing In/Ag electrodes using magnetron sputtering on the two ends of the etched ZnO MW with an electrode space of 50 μm.

The gas sensors were tested in a shielding chamber. NO_2 gas diluted in dry air was introduced into the chamber and the flow rate was kept at 100 sccm. The gas sensors' resistances were measured in an electrical measurement system (DS345, SR570, and PCI-6259) [9]. UV light (λ = 365 nm) was introduced into the chamber through a silica window.

Here, gas sensors' sensitivity is defined as $S = (R_g - R_a)/R_a$, where R_a is the stable resistance in dry air and R_g is the final resistance in NO_2 gas. The response time (τ_r) and recovery time (τ_d) are defined

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as the time required for the resistance to attain 63% ($1 - e^{-1}$) change upon introducing and removal of NO_2 gas, respectively.

3. Results and discussion

The SEM images of ZnO MWs before and after being etched for 20 s are represented in Fig. 1(a, b). The as-synthesized ZnO MW is a smooth hexagonal prism with the section's side length of ~4 μm. After being etched, the surface of the ZnO MW becomes rough and the diameter decreases to ~2 μm. The MW's specific surface area increases to ~284% of its original value (Fig. S1). This suggests the increase of surface defects such as single ionized oxygen vacancies (V_O^+), which are preferential adsorption sites for gas molecules such as O_2 and NO_2 [10,11]. To confirm it, cathodoluminescence (CL) spectra measurement of ZnO MWs is carried out. The results (Fig. 1(c)) exhibit an ultraviolet emission band (UVEB) and a green emission band (GEB), which corresponds to the band edge emission, and V_O^+ [10], respectively. The 8.83 times increased ratio of I_{GEB}/I_{UVEB} after the etching process suggests the same increased preferential adsorption sites. Notably, the increase of the preferential adsorption sites is much larger than that of the specific surface area. So, the etching improves not only the specific surface area, but also oxygen vacancies' surface density.

Gas sensors were fabricated using the individual ZnO MWs before and after being etched. Fig. 2(a, b) show their response curves towards 20 ppm of NO_2. Their resistances increase upon exposing NO_2 gas, indicating the carriers are trapped by the adsorbed NO_2 molecules. Their sensitivities are calculated to be 3.6% and 71.8% for the original ZnO MW and the etched ZnO MW based gas sensor, respectively. Thus, a ~20-fold increase of sensitivity is achieved by surface etching. Notably, ZnO MWs' resistances increase by a factor of ~200 after being etched. This is caused by the largely increased specific surface area: a large amount of oxygen molecules will adsorb onto the rough surface and combine with free electrons in the MWs to form O_2^-, which will greatly deplete the free electrons and increase the MWs' resistances [12].

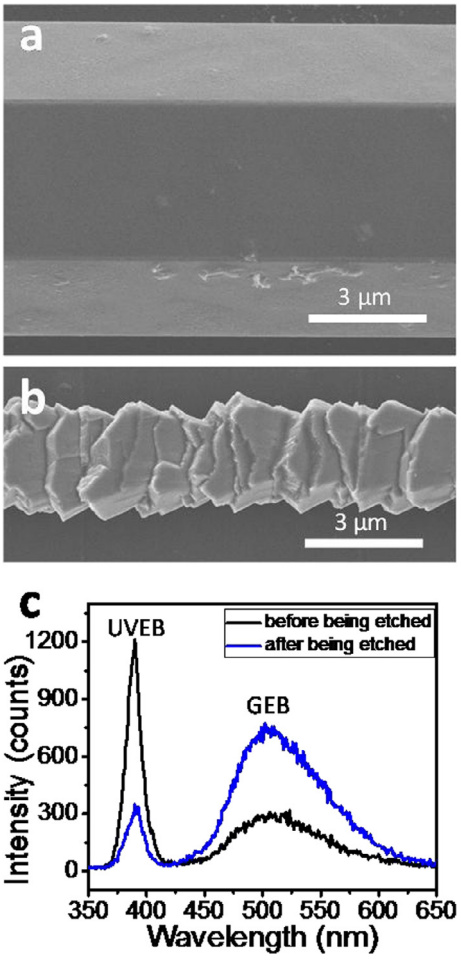

Fig. 1. SEM images of the ZnO MW (a) before and (b) after being etched. The etching time is 20 s. (c) CL spectra of the ZnO MW before and after being etched.

More detailed relation between the sensitivity and etching time is shown in Fig. 2(c), based on the response curves of the gas sensors with different etching time (Fig. 2(a, b) and Fig. S2). A constant increase of the sensitivity is observed. Thus, the sensitivity of the gas sensor can be adjusted by the etching time.

Fig. 2d shows the dynamic response of the gas sensor fabricated with the individual ZnO MW etched for 20 s. The curve illustrates that the sensor responses and recoveries to a wide range of NO_2 concentration (10–50 ppm). Based on the declaration by Occupational Safety and Health Administration, USA, the IDLH (Immediately dangerous to life or health) concentration of NO_2 gas is 20 ppm [13]. Thus, the gas sensor's detecting range covers the desired concentration for health damage. However, it takes the long response (~60 min) and recovery time (~240 min) of the gas sensor, which hinders its application.

To solve the problem, UV light with different intensity was used to illuminate the MW based gas sensor during its working time (Figs. S3 and S4). Continuous increase for the sensor's sensitivity and continuous decrease for its response and recovery times versus UV intensity (0–148.8 μW cm^{-2}) were observed. The response curve of the gas sensor fabricated with individual etched MW towards different concentrations (10–50 ppm) of NO_2 under 148.8 μW cm^{-2} of UV light is shown in Fig. 3(a). The sensitivity of the gas sensor under UV illumination shows an obvious increase than that in dark condition (Fig. 2(d)) in the whole concentration's range. Typically, the sensitivity with UV illumination increases 5.7 times (reaching 411%) compared to that without UV illumination towards 20 ppm of NO_2. The increase of the sensitivity may be ascribed to the increased adsorption sites for NO_2 due to a portion of oxygen molecular ions [O_2^-] are desorbed by UV light [14], which provides more unoccupied V_O^+.

Fig. 3(b) shows the response and the recovery time in dark condition ($\tau_{r,\ w/o\ UV}$ and $\tau_{d,\ w/o\ UV}$) and under UV illumination ($\tau_{r,\ under\ UV}$ and $\tau_{d,\ under\ UV}$) at room temperature. It's observed that $\tau_{r,\ under\ UV}$ and $\tau_{d,\ under\ UV}$ are smaller than those in dark condition. Typically, τ_r decreases from 1132 s in dark condition to 221 s (~20% of the original value) under UV illumination, and τ_d decreases from 5210 s to 118 s (~2% of the original value) for 20 ppm of NO_2. UV light speeds up the reaction between NO_2 and the electrons in ZnO by producing $O_2^-(h\nu)$, which are weakly bound to ZnO and can be easily removed [15]. This leads to the reduced response and recovery times.

So the combined technical process of surface etching and UV illumination has been developed to greatly increase the sensitivity of ZnO MW gas sensor, and speed up the response and recovery rate.

4. Conclusions

The method of surface etching towards ZnO MWs was developed to synchronously improve the specific surface area and oxygen vacancies' surface density. As a result, the individual ZnO MW gas sensor's sensitivity towards 20 ppm of NO_2 increases from 3.6% to 71.8%. What's more, the sensitivity can be adjusted by simply controlling the etching time. The etched ZnO MW based gas sensor

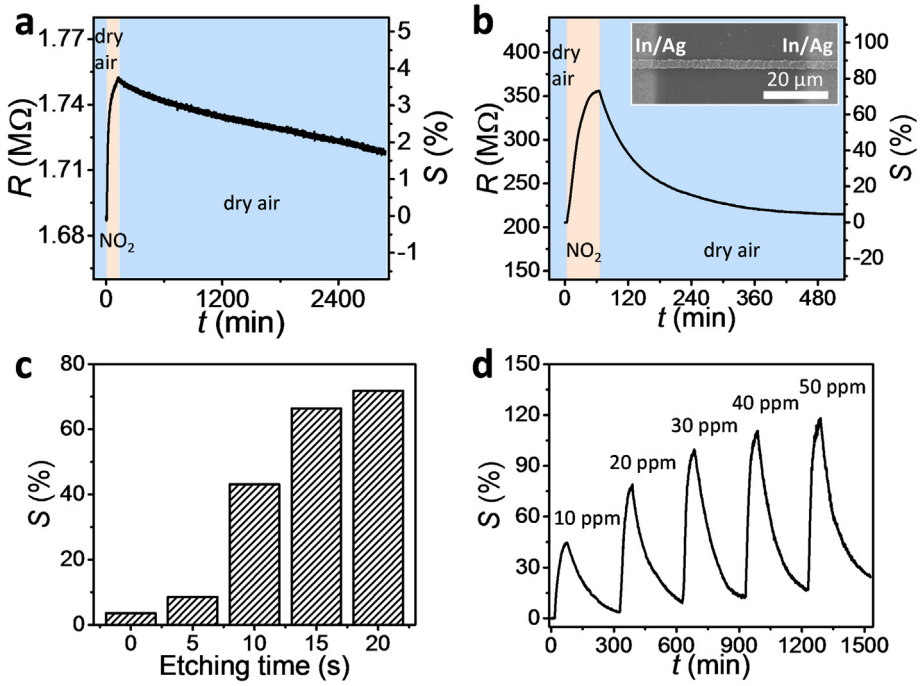

Fig. 2. The response curves of the gas sensors fabricated with the ZnO MW (a) before and (b) after being etched to 20 ppm of NO_2. (c) The relation between the gas sensor's sensitivity (S) and the etching time. (d) The dynamic response curve of the gas sensor fabricated with the ZnO MW being etched for 20 s towards different concentrations of NO_2.

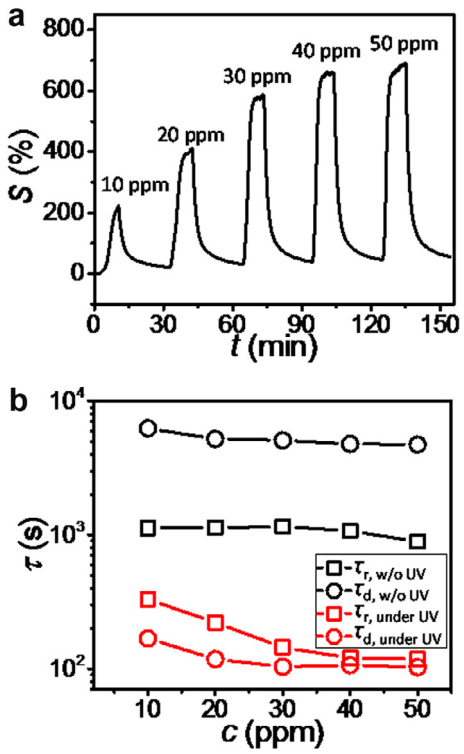

Fig. 3. (a) The dynamic response curve and (b) the calculated response/recovery time (τ) of the gas sensor towards different concentrations of NO_2 under UV illumination (UV intensity: 148.8 μW cm^{-2}).

shows room temperature sensing ability towards NO_2 under UV illumination, due to the largely improvement of the sensitivity, the response speed, and the recovery speed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2017.10.102.

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