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Synthesis of ZnO nanosheets arrays with exposed (100) facet for gas sensing applications

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ZnO nanosheets (NSs) arrays have been synthesized by a facile ultrathin liquid layer electrodeposition method. The ion concentration and electrode potential play important roles in the formation of ZnO NSs arrays. Studies on the structural information indicate that the NSs are exposed with (100) facet. The results of Raman and PL spectra indicate that there existed a large amount of oxygen vacancies in the NSs. The gas sensing performances of the ZnO NSs arrays are investigated: the ZnO NSs arrays exhibited high gas selectivity and quick response/recovery for detecting NO₂ at a low working temperature. High binding energies between NO₂ molecules and exposed ZnO (100) facets lead to large surface reconstructions, which is responsible for the intrinsic NO₂ sensing properties. In addition, the highly exposed surface and large amount of oxygen vacancies existing in the NSs also make a great contribution to the gas sensing performance.

2 Experimental

2.1 Synthesis of ZnO NSs arrays

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All the chemicals were analytical grade reagents without further purification. The electrolyte solution of 0.04 M Zn(NO$_3$)$_2$ was prepared by Millipore water. The growth system consisted of a growth chamber, a low temperature cycle water bath, a DC power supply (DF1731S85A), an arbitrary function generator (AFG 310), an optical microscope (Leica Dmlm) and a CCD camera (A311f). A Peltier element attached to DC power supply was fixed in the center of the growth chamber, which was used to rapidly adjust the electrolyte temperature. The growth chamber temperature was controlled by low-temperature cycle water bath, and the growth potential was supplied by an arbitrary function generator. The growth process could be observed by the optical microscope and CCD camera.

Firstly, silicon substrates (WaterNet Co., Type N, 0.5 mm thick, orientation [100], resistivity 2-5 Ω/cm) were cut into pieces about 20 × 20 mm$^2$ before using. And secondly, they were completely cleaned with acetone, chloroform, ethanol, and Millipore water for 10 min respectively in the ultrasonic circumstance and then blown dry with high-purity nitrogen. Finally, they were treated with an oxygen plasma for 3 min at 300 W (Templa System 100-E plasma system) and rinsed again with Millipore water. The surface of silicon substrates became fully hydrophilic after above procedure. Surface structures with -CH$_3$ termination were carried out by immersing the silicon substrate into a 1mm OTS (APTMS, Aldrich) solution of 1-phenyloctane (Aldrich) or hexadecane (Aldrich) for 15 min in the ultrasonic condition, and then were rinsing in chloroform to remove the polymeric residuals. Subsequently, the silicon wafer was placed on the Peltier element while two parallel electrodes made of a 30 µm thick Zn foil were put on silicon substrates and separated by a distance of approximately 8 mm. Then the solution was dropped on the silicon substrate. Finally, a cover glass was carefully put on the two electrodes and then filled the space between the cover glass and silicon substrate with solution. A uniform ultra-thin ice layer could be formed between the silicon substrate and cover glass by adjusting the temperature of the Peltier element and the low-temperature cycle water bath. After an ultra-thin ice layer was formed, we kept the growth chamber temperature constant for 30 min. The ultrathin liquid layer of concentrated electrolyte was formed between the ice layer and upper surface of silicon substrate, as well as the ice layer and lower surface of cover glass. Electrodeposition was initiated when a constant voltage of 0.8 V was applied on the parallel electrodes. As the growth process ended, a slight increase in temperature was provided by the Peltier element to melt ice. Then the cover glass and silicon substrate were taken out to clean by the deionized water and dried at room temperature. The growth process was displayed in the supplementary information.

2.2 Characterization and gas-sensing measurement

The morphology and crystal structure of the ZnO NSs arrays were characterized by scanning electron microscope (SEM FEI Magellan-400), X-ray diffraction (XRD, Rigaku D/max-Ra) and transmission electron microscopy (TEM, JEOL JEM-2200FS) respectively. Transmission spectra were recorded on the HR-800 Lab Ram Infinity spectrophotometer which was carried out with a continuous He-Cd laser with the excitation wavelength of 325 nm and UV-3150 spectrophotometer, respectively. Room temperature Raman spectrum and PL spectrum were recorded on a HR-800 LabRam Infinity spectrophotometer excited by a continuous He-Cd laser with respective excitation wavelengths of 325 nm.

The samples on the cover glass were used as the test objects. At first, the samples were covered by a linear mask with a width of 50 µm. Two copper wires were fixed on both sides of the mask separately. Then the Au film was deposited on the glass by vacuum ion sputtering for 300 s. After that, the mask was taken away, and the NSs arrays were connected into the circuit. During the measurement, the electrical signals were measured and recorded by a Keithley 2400 sourcemeter (2400, Keithley, USA) and a Digital Phosphor Oscilloscope (TDS5034B, Tektronix, USA). The working temperature was controlled by a flat heating plate with a temperature controller. The desired concentrations of the testing gases were obtained by the static gas distribution method, which was calculated by the following formula:

$$Q = \frac{V \times \phi \times M}{22.4 \times d \times p} \times 10^{-6} \times \frac{273 + T_s}{273 + T_0}$$

(1)
3 Results and Discussion

3.1 Structure, morphology and optical properties

Fig. 1a and b display the SEM images of ZnO NSs arrays with low and high magnification, and the insert image (in Fig. 1b) displays the cross-sectional view of the NSs arrays. The images illustrate that the ZnO array is interwoven by abundant NSs with an average thickness of 20 nm. The unique NSs arrays with external inter-space between each NS can provide an extensive pore network for gas diffusion.

To gain the component and structure information of ZnO NSs arrays, XRD, TEM and spectrum experiments were conducted. The XRD pattern of ZnO NSs arrays is shown in Fig. 2a. All the diffraction peaks match to those characteristic of the wurtzite ZnO structure (JCPDS 036-1451). No characteristic peaks of other chemical compounds were observed such as Zn or Zn(OH)₂, indicating that the electrodeposition product is pure ZnO. Fig. 2b depicts the transmission spectrum and its derivative curve of the ZnO NSs arrays. Only one distinct peak is observed at about 3.24 eV in derivative curves, which arises from the ZnO near-band-edge (NBE) absorption. Further structural characterizations of the as-synthesized nanodeposits were performed with TEM. Fig. 3a shows a TEM image of the individual ZnO NS. The HR-TEM analysis of an individual NSs shows that the ZnO array is interwoven by abundant NSs with an average thickness of 20 nm. The unique NSs arrays with external inter-space between each NS can provide an extensive pore network for gas diffusion.

The gas-sensing mechanism of semiconductor gas sensors is generally based on the adsorption and reaction of gas molecules on the material surface, where oxygen deficiency plays an important role. Usually, the Raman and PL spectra are carried out to analyse the defects of semiconductor materials due to their higher sensitivity to crystal imperfections. Fig. 4a displays that the typical PL spectrum indicating two bands at 379 and 522 nm. The ultraviolet (UV) peak nears 380 nm can be attributed to the conduction band to valence band (CB-VB) combination according with the result of transmission spectrum in Fig. 2b. The green PL near 500 nm is usually ascribed to oxygen vacancy and the yellow or orange PL (near 600 nm) is related to oxygen interstitial. The two peaks of Raman spectrum at 441 and 566 cm⁻¹ shown in Fig. 4b are assigned to the E₂L₃ and E₁₇ vibrational modes of the ZnO, respectively. The E₂L₃ mode involves oxygen atoms, and the E₁₇ mode is associated with oxygen deficiency indicating that oxygen vacancies exist in the NSs. The broad features of 566 cm⁻¹ peak in the Raman spectra and the high intensity 500 nm band in the PL spectrum indicate that ZnO NSs are significantly deficient in oxygen. According to the above analyses, there exists large amounts of oxygen vacancies in the ZnO NSs arrays.

3.2 Gas-sensing properties

Based on as-prepared ZnO NSs arrays, we fabricate chemical sensors and investigate their gas sensing performances. The
gas-sensing properties are heavily affected by the working temperature, as this factor greatly influences the surface state of sensing materials. Therefore, in order to investigate the influence of the operating temperature and to find an optimum operating temperature of the sensors, the sensitivities of the as-prepared ZnO nanostructures toward 100 ppm of NO\textsubscript{2} as a function of working temperature are tested and the results are shown in Fig. 5. It can be observed that the sensitivity of the ZnO NSs sensor increases gradually while the working temperature rises from 120 to 180 °C and reaches a maximum value of R= 20 at 180 °C. A further increase of the operating temperature above 180 °C, however, results in a gradual decline in the sensitivity of the sensors. Thus, the operating temperature of 180 °C is the optimal temperature for NO\textsubscript{2} detection, so it is chosen as the working temperature to further examine the characteristics of the sensor. Compared with the NO\textsubscript{2}-sensing properties of other ZnO-based nanostructures\textsuperscript{19-22}, sensor in this work exhibits lower or comparable working temperature.

Fig. 5 Gas response of ZnO NSs film to 100 ppm NO\textsubscript{2} as the function of the operating temperatures.

Fig. 6 Responses of ZnO NSs film to 100 ppm various testing gases.

Besides, we further examine other gas-sensing properties including selectivity, detection limit, stability, response and recovery time, which are important parameters for the gas sensor in practical applications. Fig. 6 shows the selectivity of the ZnO NSs sensors to NO\textsubscript{2} relative to H\textsubscript{2}S, ethanol, benzene, acetone, methanol, methanal, toluene and NH\textsubscript{3} at the same gas concentrations (100 ppm). The gas sensing response to NO\textsubscript{2} is much higher than other gases, suggesting that the obtained ZnO NSs arrays have high selectivity for NO\textsubscript{2}. Fig. 7a illustrates that the responses of sensor based on ZnO NSs as a function of NO\textsubscript{2} concentration from 1 to 400 ppm. In the low concentration range from 1 to 100 ppm, we observe that the sensitivity is approximately linear increase with increasing NO\textsubscript{2} concentration (shown in the insert of Fig. 7a). Above 100 ppm, the sensitivity changes slowly with the variations of the NO\textsubscript{2} concentration, which indicates that the sensor is near saturation. Furthermore, the stability of the gas sensors is also a crucial point for the practical application of the gas sensors. Fig. 7b depicts the representative dynamic responses to different NO\textsubscript{2} concentrations (1-400 ppm) at 180 °C, respectively. The response transient of ZnO NSs sensor to 50 ppm NO\textsubscript{2} is shown in Fig. 8a. The four sequential cycles of response transients show that a reversible, repeatable and stable characteristic. The transient response of ZnO NSs to 10 ppm NO\textsubscript{2} is shown in the inset of Fig. 8a. The results indicate that the sensor responds immediately when NO\textsubscript{2} gas is introduced and then rapidly recovers to initial value after the NO\textsubscript{2} releasing. The respective response and recovery times of ZnO NSs sensors are around 3 and 12 s. Compared with the NO\textsubscript{2} sensing properties of other ZnO-based nanosystems\textsuperscript{19-24}, sensor in this work exhibits comparable or wider detection limits but faster response and recovery time, which is due to
the specific structure of these ZnO NSs with a greater surface area and highly exposed surface.

3.3 NO$_2$-sensing mechanism

It is crucial to understand the sensing mechanism for designing NO$_2$ sensors of high sensing performances. As metal oxide ZnO exposed to air, oxygen molecules will be adsorbed on the oxide surface and then extract electrons in the bulk, leading to a narrow conduction channel. When the n-type semiconductor ZnO is exposed to NO$_2$ gas the NO$_2$ molecules can not only capture electrons from the ZnO conduction band but also react with the chemisorbed oxygen on the surface, which results in withdrawing of electrons from the surface, depleting them from the conduction band, and leading to an increase in resistance (Eq. 2 and 3). When the semiconductor oxide is exposed to air again, NO$_2$ reacts with hole release electrons into the conduction band, leading to NO$_2$ being released into the air and reducing resistance (Eq. 4). The adsorption and desorption occur on the ZnO surface according to the following chemical reaction:

\[ \text{NO}_2(g) + e^- \rightarrow \text{NO}_2(ads) \]  
\[ \text{NO}_2(g) \rightarrow \text{NO}_2(ads) + 2e^- \]  
\[ \text{NO}_2(ads) + h^+ \rightarrow \text{NO}_2(g) \]  

The kinetics process of gas adsorption and desorption can be understood as follows: When the NO$_2$ gas flows through the sensor element, the adsorption speed of NO$_2$ on the sensor surface is very fast, indicated by the steep slope of the response process. This suggests that the adsorption process plays a dominant role during the initial sensing stage. As the sensing process goes on, the adsorption of the NO$_2$ gas slows down gradually. When the gas adsorption and desorption reach equilibrium, the resistance increases to the maximum value. In contrast, desorption of NO$_2$ gas dominates the sensing process when the NO$_2$ flow is stopped, resulting in the return of the sensor signal to the baseline.

The electron exchange between the surface states and the bulk takes place within a surface layer whose width is about $\lambda_D$ (Debye length). The value of $\lambda_D$ can be calculated by the following equation:

\[ \lambda_D = \left( \frac{kT}{q^2n_e} \right)^{1/2} \]  

where $\varepsilon$ is the static dielectric constant; $\kappa$ is the Boltzmann’s constant; $T$ is the absolute temperature; $q$ is the electrical charge of the carrier and $n_e$ is the carrier concentration. For bulk ZnO, $\lambda_D$ is about 20 nm at 180 °C according to the above equation as $n_e$ is assumed to be 5x10$^{16}$ cm$^{-3}$. Thus, the thickness of the ZnO NSs is comparable to the Debye length which could effectively enhance the gas sensing performance. It is recognized that the reaction of NO$_2$ on gas sensing materials is expected to occur mainly via electron transfer and variation of oxygen species on the surface. Considering that the electrical properties of the semiconductor oxides are significantly influenced by the native defects or the nonstoichiometry. Chemisorbed NO$_2$ binds more strongly to the oxygen vacancy site, which exist on the ZnO (100) surface, with higher binding energies greater than clean stoichiometric ZnO (100) surface. Large surface reconstructions around the oxygen vacancy site can take place after NO$_2$ adsorption, which can lead to large electrical resistance variation. On the other hand, such a rapid sensing performance can be ascribed to be the special NSs arrays structure in which the gas adsorption and desorption would be remarkably improved by the highly exposed internal spaces among the NSs. Meanwhile, most of the active sites in the sensing layer consists of ZnO NSs can be effectively utilized for contact reactions, resulting in remarkably improved response, lower working temperature and shorter response and recovery time.

4 Conclusions

The hierarchical ZnO arrays assembled from 2D NSs with exposed (100) facets are synthesized through a facile ultrathin liquid layer electrodeposition method. PL and Raman spectra gas-sensing results reveal that the NSs-assembled ZnO arrays exhibit excellent NO$_2$ gas sensing performance evidenced by high response, small cross sensitivity, fast response/recovery (3 s and 12 s) and low operating temperature (180 °C), suggesting their potential applications as advanced gas sensing materials. The excellent performance in sensing can be attributed to the specific morphology of the NSs arrays and the thin NSs exposed with (100) facet. In addition, there exists amount of oxygen vacancies in ZnO NSs which is benefit for its gas sensing performance. This present work will provide a deeper understanding of the sensing mechanism of ZnO-based sensors, and motivates us to further fabrication of other nanomaterials with specially exposed crystal surfaces for promising applications in gas sensors, photocatalysts and more.

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Notes and references