

ZnO Nano/Microwires Ethanol Sensors: Role of TiO₂ Additive

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Abstract

ZnO nano/microwires (ZnO-NMWs) with varying TiO₂ additions (0 – 30 mol% TiO₂) were synthesized at temperatures ranging from 600 – 800°C for 12 h via a simple thermal oxidation reaction method in a normal atmosphere. The characterizations of the ZnO-NMWs were carried out, and it was found that the greatest quantity and longest ZnO-NMWs were observed at a heating temperature of 600°C. The heating temperature significantly influenced the quantity and dimensions of the ZnO-NMWs. The formation of the fcc-Zn₂TiO₄ phase was distinctly identified using XRD and Raman analyses, and an increased proportion of the Zn₂TiO₄ phase was achieved with elevated heating temperatures. The ZnO-NMWs, synthesized at 600°C with varying TiO₂ additives, were applied as ethanol sensors, and their ethanol sensing properties were investigated. An improvement of sensor response due to TiO₂ addition can be attributed to the reduction in electron concentration within the sensor, resulting from the formation of Zn₂TiO₄ phase. The NWs-TiZnO-30 sensor shows the highest sensing response of 9.30 at 360°C. Consequently, the incorporation of TiO₂ with ZnO-NMWs is a promising method for improving sensor response.

Keywords: Nanostructured materials; Thermal oxidation; Additive; Gas sensor; ZnO

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1. Introduction

One-dimensional nanostructures, including nanobelts, nanowires, and nanoribbons, have attracted key research interest in the past few years. Interest in these nanomaterials arises from their unique properties and potential performance compared to their bulk counterparts. Nowadays, metal oxide semiconducting nanowires have been intensively studied due to their great potential properties [1 – 5]. Among these, a promising material, ZnO nanowires, has been used in diverse applications such as biosensors, dye-sensitized solar cells, field-effect transistors, field emission devices, and gas sensors [1, 5 – 10]. Extensive current research indicates that these practical applications will be commercially used in the forthcoming years.

Several methods were employed to improve the sensing properties of gas sensors. Certain researchers deposited catalytic metals onto the sensor surface, enhancing reaction rate and/or the quantity of adsorbed oxygen species [11 – 13]. In addition, controlling architectural defects in sensing materials is another way for tuning the sensing property [3]. Recently, metal/metal oxide additions have been recognized as promising candidates for enhancing gas sensing response improvement by modifying the electrical state of the sensor surface, including materials such as Ru, Gd, Ti, and TiO₂ [14 – 17]. The Ti-coated ZnO nanostructure sensor, fabricated via electron beam evaporation, demonstrated an improved toluene sensing response compared to the uncoated ZnO nanostructure sensor [18]. Indeed, our group demonstrated that adding TiO₂ to ZnO tetrapods improved their ethanol and carbon monoxide sensing responses [7, 11, 17].

In this work, ZnO nano/microwires were synthesized using a simple thermal oxidation reaction method, both with and without TiO₂ addition. The properties of the nano/microwires were carried out, and their ethanol sensing response was examined to assess the impact of the TiO₂ addition on the sensing performance.

2. Materials and Methods

2.1 Materials and Methods

ZnO nano/microwires (ZnO-NMWs) with varying TiO₂ additives were synthesized by using the simple thermal oxidation reaction method. Zn powder (99.90%, Univar) was mixed and milled with 0, 10, 20, and 30 mol% of anatase TiO₂ (a-TiO₂) powder (99.80%, Sigma-Aldrich). The straightforward thermal oxidation reaction approach presents benefits compared to alternative methods, chiefly because of its reduced expense and ease of use. Furthermore, this technique produces a substantial yield of nano/microwire structures. The ground powder was combined with 5 wt.% polyvinyl alcohol (PVA) to form a paste, which was subsequently screened onto a cleaned alumina substrate. The thick films were dried in ambient air for 24 h and thereafter heated at 600 – 800°C in a tube furnace for 12 h in ambient air to facilitate the oxidation reaction. Subsequently, the furnace was allowed to cool naturally to room temperature, and the ZnO-NMWs thick films were obtained. These were denoted as NWs-ZnO, NWs-TiZnO-10, NWs-TiZnO-20, and NWs-TiZnO-30, representing 0, 10, 20, and 30 mol% of TiO₂ powder, respectively. The obtained products were characterized by field emission scanning electron microscopy (FE-SEM), energy dispersive spectrometry (EDS), X-ray diffractometry (XRD), and Raman spectroscopy (RS) to determine surface morphology, chemical content, phase development, and crystal structure.

2.2 Thick Film Sensor Preparation and Ethanol Gas Sensor Investigation

The synthesized ZnO-NMWs thick films were fabricated as ethanol sensors by applying Au electrodes on the top of the surface with Au paste. The ZnO-NMWs thick film sensor was dried in ambient air for 6 h and then annealed at 500°C for 4 h. The nickel-chromium coil heater was subsequently positioned beneath the alumina substrate. The sensor resistance was recorded using a volt-amperometric technique interfaced to a computer. The ethanol gas was generated from an ethanol solution with an alcohol simulator (GUTH Laboratory, Inc., Harrisburg, USA). The alcohol simulator operated to simulate alcohol concentration in a setting similar to exhaled human breath. Fig. 1 illustrates the schematic diagram of the ethanol sensing system.

The ZnO-NMWs thick film sensing characteristics were studied with an ethanol concentration of 1,000 ppm at 260 – 360°C. The sensing response (S_g) was defined in Eq. (1), where R_{air} is a sensor resistance in air and R_{gas} is its resistance in ethanol-air mixed gas [11, 17].

$$S_g = \frac{R_{air}}{R_{gas}} \quad (1)$$

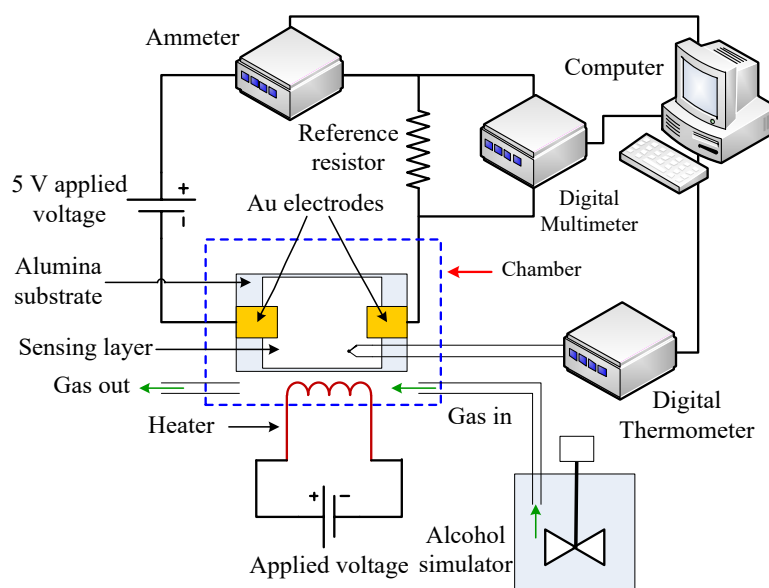


Fig. 1 The schematic diagram of the ethanol sensing system.

3. Results and Discussions

3.1 Morphological, Phase and Chemical Analysis

FE-SEM images in Fig. 2 reveal that the ZnO-NMWs thick films mainly consisted of sharp-tipped nano/microwires growing outward from microparticles. The refined ZnO-NMWs with various TiO_2 additives, synthesized at 600°C , were clearly depicted on the left side of Fig. 2(a, d, g, and j). Upon reaching a temperature of 800°C , many nano/microstructures of limited length were observed, as shown on the right side of Fig. 2(c, f, i, and l). The length and diameter of the ZnO-NMWs ranged from $0.30 - 30\ \mu\text{m}$ and $0.10 - 1.80\ \mu\text{m}$, respectively. The highest quantity and greatest lengths of ZnO-NMWs were observed at a heating temperature of 600°C . These results indicated that the heating temperature significantly influenced the quantity and dimensions of the ZnO-NMWs. These results align with our prior publications on the growth mechanism of nano/microwires via the thermal oxidation reaction approach [19, 20].

Fig. 3 presents high magnification FE-SEM images of the nano/microwires: (a) NWs-TiZnO-30 synthesized at 600°C and (b) NWs-TiZnO-30 synthesized at 800°C . Additionally, the EDS spectrum of the NWs-ZnO and NWs-TiZnO-30 synthesized at 600°C was carried out and shown in Fig. 3(c) and (d), respectively. The EDS spectra in Fig. 3(c) shows indications for Zn (45.45 atomic%) and O (54.55 atomic%). In contrast, the EDS spectrum depicted in Fig. 3(d) exhibited indications for Zn (44.94 atomic%), O (49.24 atomic%), and Ti (5.82 atomic%). The Ti signal was detected in NWs-TiZnO-30; however, no Ti signal was observed in NWs-ZnO sample. In addition, an Au signal was also detected in the EDS spectra of both samples. This Au signal originated from the Au coating film

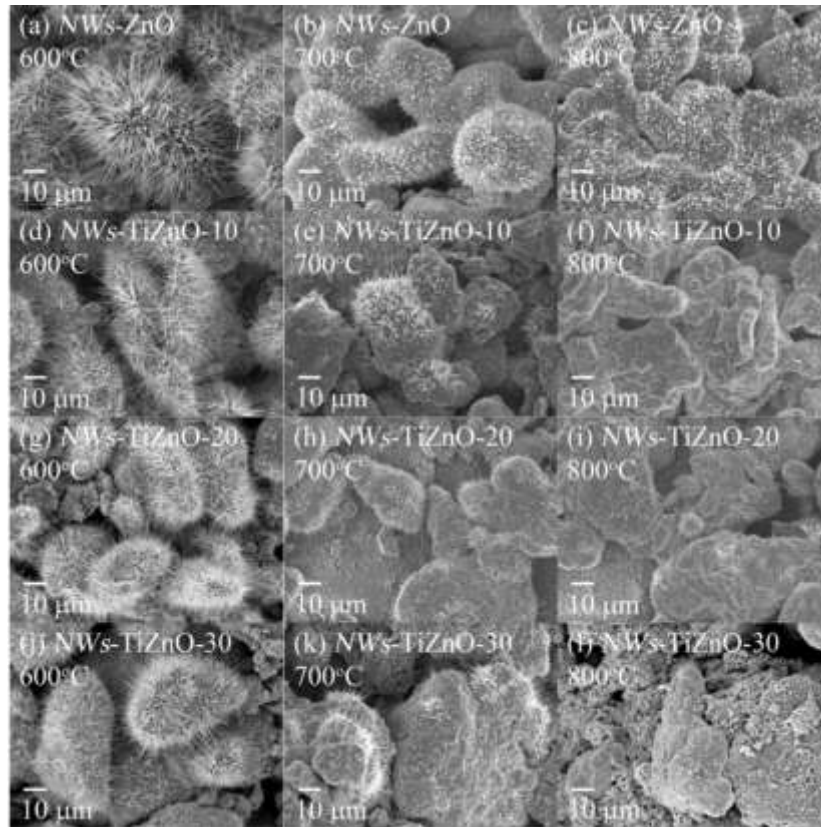


Fig. 2 FE-SEM images of nano/microwires with various synthesized temperatures for (a-c) NWs-ZnO, (d-f) NWs-TiZnO-10, (g-i) NWs-TiZnO-20, and (j-l) NWs-TiZnO-30, respectively.

Typical XRD patterns of the ZnO-NMWs with different TiO_2 additives synthesized at 700°C were shown in Fig. 4(a). It was clearly seen that the NWs-ZnO sample showed the peaks corresponding to a hexagonal wurtzite ZnO structure (JCPDS no. 36-1451). Beside the ZnO peaks, XRD patterns of the ZnO-NMWs containing TiO_2 additive displayed a face-centered cubic (fcc) Zn_2TiO_4 phase (JCPDS no. 86-0155). The intensity of Zn_2TiO_4 peaks increased, whereas the intensity of

ZnO peaks reduced with the addition of TiO_2 . The formation of the fcc- Zn_2TiO_4 phase is in good agreement with previous reports [21]. The formation of the Zn_2TiO_4 phase with ZnO occurred at TiO_2 additive concentrations below 33 mol% and within a temperature range of 400 – 1,537°C.

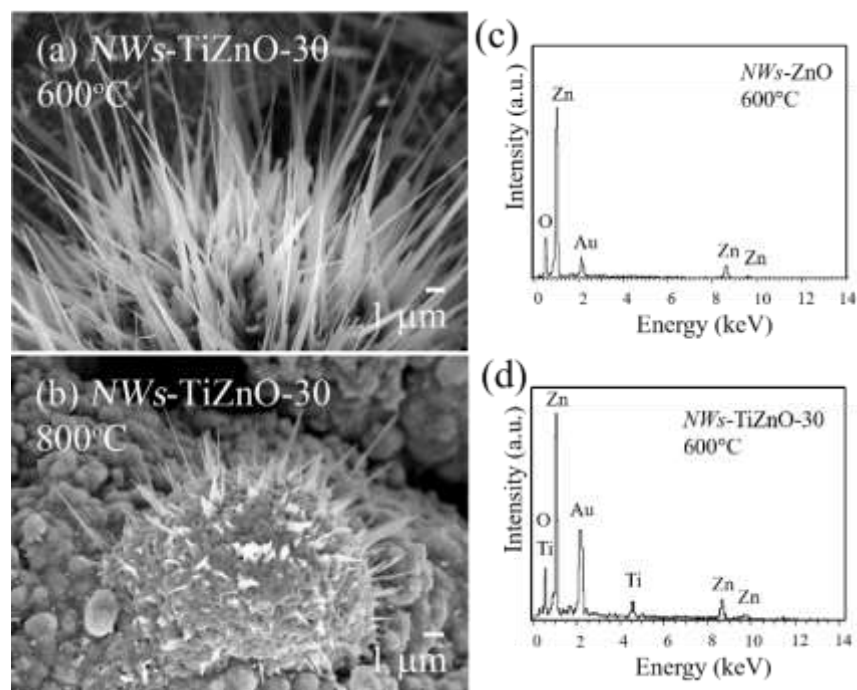


Fig. 3 High magnification FE-SEM images for (a) NWs-TiZnO-30 synthesized at 600°C and (b) NWs-TiZnO-30 synthesized at 800°C; EDS spectrum for (c) NWs-ZnO and (d) NWs-TiZnO-30 synthesized at 600°C.

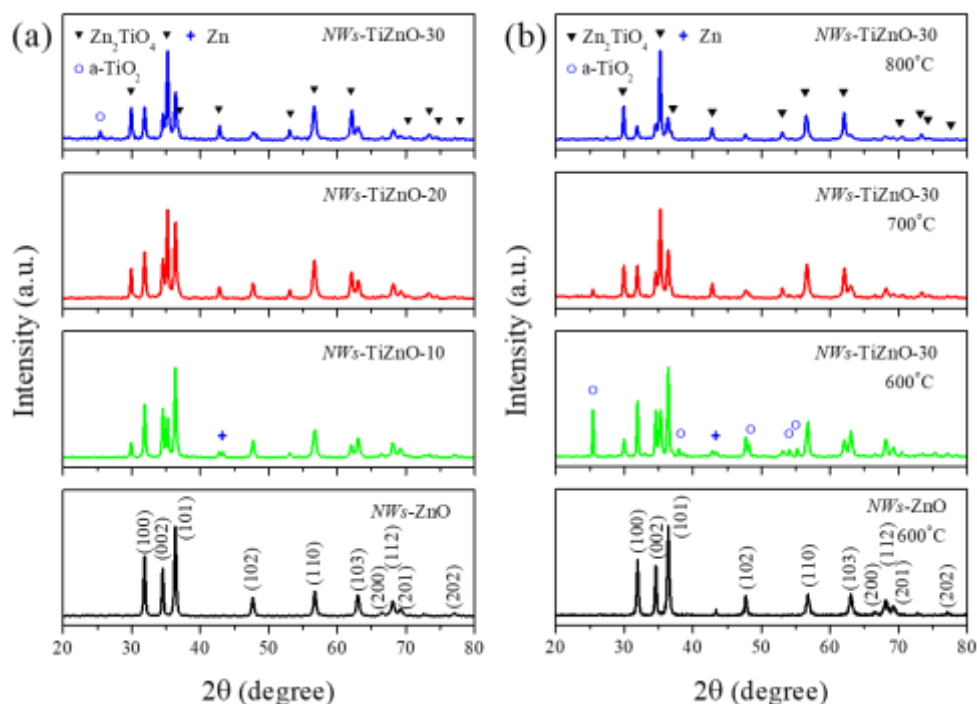


Fig. 4 XRD patterns for (a) nano/microwires with varying TiO_2 additive synthesized at 700°C and (b) NWs-TiZnO-30 synthesized at 600°C, 700°C, and 800°C, respectively, compared with NWs-ZnO synthesized at 600°C.

Fig. 4(b) presents the XRD patterns of NWs-TiZnO-30 at various heating temperatures in comparison with NWs-ZnO synthesized at 600°C. At 600°C, the ZnO and Zn₂TiO₄ peaks were observed, accompanied by low intensity peaks of Zn and a-TiO₂. The residual Zn phase resulted from partial oxidation of Zn at low temperatures, which was not observed at temperatures beyond 700°C. With the rise in temperature, the intensity of the Zn₂TiO₄ peaks increased, in contrast to the peaks of ZnO, a-TiO₂, and Zn. Similar results were observed with all TiO₂ additives. Besides XRD results, Raman spectroscopy was used to analyze crystal defects, and the Raman spectra were shown in Fig. 5. The observed vibration modes in the NWs-ZnO spectrum in Fig.5(a) at 332, 388, 412, 438, 533, and 585 cm⁻¹ corresponded to ZnO phase of E₂(H)-E₂(L), A₁(TO), E₁(TO), E₂(H), A₁(LO), and E₁(LO), respectively [8]. No defects or additional impurity peaks were observed in the spectra. This result revealed that NWs-ZnO exhibited a high degree of crystallinity. For the ZnO-NMWs with different TiO₂ additives, in contrast, the presence of Zn₂TiO₄ phase was further confirmed by Raman spectra, as illustrated in Fig. 5(b, c, and d). The Raman peaks at 229, 264, 310, 344, and 716 cm⁻¹ corresponded to Zn₂TiO₄ phase of F¹_{2g}, F²_{2g}, E_g, F³_{2g}, and A_{1g} in space group O⁷_h [22].

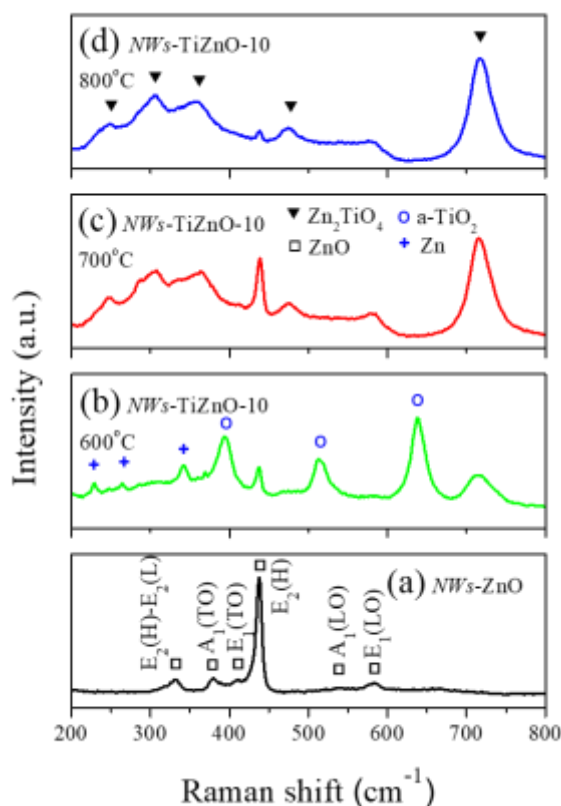


Fig. 5 Room temperature Raman spectra of NWs-TiZnO-10 synthesized at various temperatures are compared with NWs-ZnO synthesized at 600°C for (a) NWs-ZnO and (b-d) NWs-TiZnO-10 synthesized at 600°C, 700°C, and 800°C, respectively.

3.2 Ethanol Sensing Properties Investigation

The ZnO-NMWs thick films, synthesized at 600°C with varying TiO₂ additives, were chosen for further examination of their ethanol sensing properties because of their high quantity and greatest length of nano/microwires. The SEM image of the ZnO-NMWs thick film was shown in Fig. 6(a). Fig. 6(b) displays the ethanol sensing response of the sensors. It can be seen that at the optimum operating temperature, the sensing response of the ZnO-NMWs thick film sensors with TiO₂ additive showed a higher value compared to that of the pure ZnO-NMWs thick film sensors [7, 11, 23], specifically 280°C for NWs-TiZnO-20 and 360°C for NWs-TiZnO-30. However, the sensing response of the NWs-TiZnO-10 sensor exhibited an exception, demonstrating a comparable sensing value. For instance, the sensing responses of the NWs-TiZnO-30, NWs-TiZnO-20, and NWs-TiZnO-10 sensors were 9.30, 2.20, and 1.30, respectively, at the optimal operating temperature. This contrasted with the value of 1.70 for the NWs-ZnO sensor. Compared to our prior ZnO tetrapod ethanol sensor [11, 17], the ZnO-NMWs thick

film sensors had a reduced ethanol sensing response. However, the ZnO-NMWs thick film can be formed in a single step directly onto the Al_2O_3 substrate during the heat treatment, which is an advantage over the ZnO tetrapod thick film fabrication.

The improvement of the sensing response attributed to the TiO_2 additive can be explained by the elevation of sensor resistance resulting from the formation of Zn_2TiO_4 phase. Figure 6(c) illustrates the sensor resistance at various TiO_2 additive concentrations as a function of the operating temperature. The sensor resistance of the NWs-ZnO and NWs-TiZnO-10 sensors was relatively low; however, the NWs-TiZnO-20 sensor exhibited increased resistance, and the NWs-TiZnO-30 sensor demonstrated the highest resistance. The lowered sensor resistance of the NWs-TiZnO-10 sensor was attributed to the residual Zn phase, as confirmed by the XRD pattern. This would result in no improvement of sensing response. Increased TiO_2 additive led to the formation of the Zn_2TiO_4 phase, which resulted in elevated sensor resistance and enhanced sensing response [23]. Furthermore, the sensor resistance can be related to the sensing response through the electron concentration of the sensor in air (n_0) as described in the sensing response formula [24]. Γ_i and $k_{\text{Eth}}(T)$ are a proportional constant and a reaction rate constant for the interaction between the adsorbed oxygen species and the ethanol vapor, both of which were dependent on the operating temperature, respectively. $O_{\text{ads}}^{\text{ion}}$ is the adsorbed oxygen species concentration, and C_g^b is the ethanol concentration, while n_0 is the electron concentration of the sensor in air.

$$S_g = \frac{R_{\text{air}}}{R_{\text{gas}}} = \frac{\Gamma_i k_{\text{Eth}}(T) [O_{\text{ads}}^{\text{ion}}]^b C_g^b}{n_0} + 1 \quad (2)$$

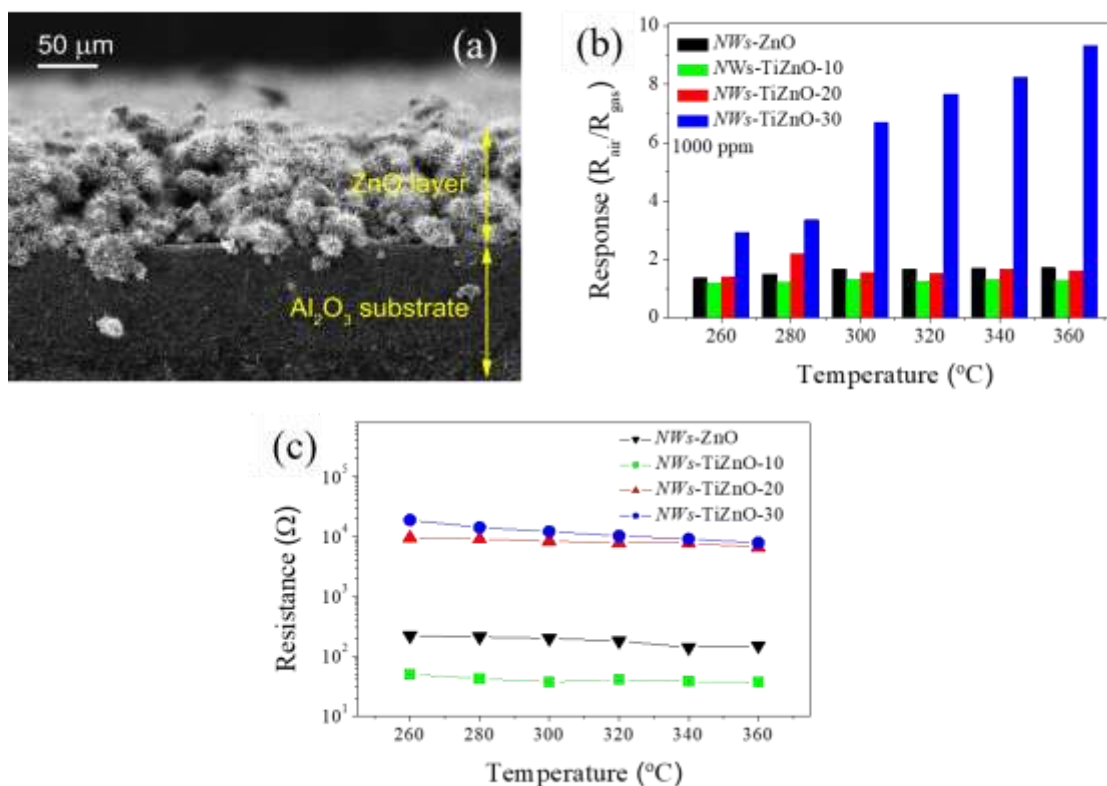


Fig. 6 (a) SEM image of the ZnO-NMWs thick film, (b) Sensing response towards 1000 ppm ethanol vapor, and (b) sensors resistance in the air.

In solid-state reaction of Zn and TiO₂ powder could be explained by the following reaction.



or



However, the XRD and Raman results indicated that the mixture was made up of ZnO, TiO₂, Zn₂TiO₄ and some Zn. Zn₂TiO₄ is a semiconductor with good grain boundary modulation expected to improve gas sensing. However, even a small amount of metallic Zn can dominate the electrical transport. The metallic Zn is a much better conductor of electricity and will form preferred current paths. It also will donate electrons to the oxide matrix. This lowers the depletion layer width and the grain-boundary potential barrier. As a result, the change in resistance caused by gas adsorption is greatly reduced. Also, the remaining Zn covers part of the active oxide surface and could oxidize even more during detection, which would make the baseline unstable. As a result, the presence of residual Zn cancels out the positive effects of Zn₂TiO₄, leading to little to no change in sensor performance.

The sensing response, as indicated in Eq. (2), is directly proportional to resistance in air and inversely proportional to the electron concentration of the sensor in air. Thus, the improvement of sensing response by the TiO₂ additive results from the reducing of electron concentration in the sensor, which is attributed to the formation of Zn₂TiO₄ phase.

4. Conclusion

The ZnO-NMWs with varying TiO₂ additives (0 – 30 mol% TiO₂) were successfully synthesized using a simple thermal oxidation reaction method in ambient air. The quantity of nano/microwires, their dimensions, phase formation, and phase fraction were significantly influenced by the heating temperature. The maximum values and the greatest quantity of the ZnO-NMWs were observed at a heating temperature of 600°C, and the higher fraction of the Zn₂TiO₄ phase was obtained with increasing heating temperature. The synthesized ZnO-NMWs with varying TiO₂ additives at a heating temperature of 600°C were effectively applied as the ethanol sensors. The ethanol sensing characteristics demonstrated an enhancement in sensing response due to TiO₂ addition. This is attributed to the decreased electron concentration in the sensor, resulting from the creation of Zn₂TiO₄ phase. Thus, incorporating TiO₂ with ZnO-NMWs represents a promising method for enhancing the sensor response. In addition, the ethanol sensing characteristics of sensors with TiO₂ additive can be simply tuned via this simple method. The ability to tune the sensor properties has implications for an electronic nose application

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