In$_2$O$_3$ Nanotower Hydrogen Gas Sensors Based on Both Schottky Junction and Thermoelectronic Emission

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Abstract

Indium oxide (In$_2$O$_3$) tower-shaped nanostructure gas sensors have been fabricated on Cr comb-shaped interdigitating electrodes with relatively narrower interspace of 1.5 $\mu$m using thermal evaporation of the mixed powders of In$_2$O$_3$ and active carbon. The Schottky contact between the In$_2$O$_3$ nanotower and the Cr comb-shaped interdigitating electrode forms the Cr/In$_2$O$_3$ nanotower Schottky diode, and the corresponding temperature-dependent I-V characteristics have been measured. The diode exhibits a low Schottky barrier height of 0.45 eV and ideality factor of 2.93 at room temperature. The In$_2$O$_3$ nanotower gas sensors have excellent gas-sensing characteristics to hydrogen concentration ranging from 2 to 1000 ppm at operating temperature of 120–275 °C, such as high response (83 % at 240 °C to 1000 ppm H$_2$), good selectivity (response to H$_2$, CH$_4$, C$_2$H$_4$, and C$_3$H$_8$), and small deviation from the ideal value of power exponent ($\beta$) (0.48578 at 240 °C). The sensors show fine long-term stability during exposure to 1000 ppm H$_2$ under operating temperature of 240 °C in 30 days. Lots of oxygen vacancies and chemisorbed oxygen ions existing in the In$_2$O$_3$ nanotowers according to the x-ray photoelectron spectroscopy (XPS) results, the change of Schottky barrier height in the Cr/In$_2$O$_3$ Schottky junction, and the thermoelectronic emission due to the contact between two In$_2$O$_3$ nanotowers mainly contribute for the H$_2$ sensing mechanism. The growth mechanism of the In$_2$O$_3$ nanotowers can be described to be the Vapor-Solid (VS) process.

Keywords: Nanotowers; Hydrogen; Gas sensor; Schottky junction; Thermoelectronic emission

Background

Chemical sensors based on semiconductor oxide materials have been extensively researched due to their advantageous features, such as high sensitivity, low cost, and simplicity in fabrication [1]. Among them, indium oxide (In$_2$O$_3$) semiconductive materials have been extensively studied as chemical sensors for a long time due to their advantageous features such as a wide bandgap around 3 eV, a low resistance, and good catalysis [2].

1-D In$_2$O$_3$ nanostructures show high gas-sensing response due to their high electric conductance, high transparency to visible light, strong interaction with the gas molecules, high surface-to-volume ratio, and large surface activities [3]. However, up to now, few In$_2$O$_3$ nanostructures exists good sensing properties to hydrogen. Hydrogen is the most attractive and sustainable energy for the future generations due to its high efficiency and renewable properties.

In this contribution, we report that new In$_2$O$_3$ tower-shaped nanostructures with high surface-to-volume ratio have been fabricated using thermal evaporation of the mixed powders of In$_2$O$_3$ and active carbon. The synthesized In$_2$O$_3$ nanotowers distributing on Cr comb-shaped interdigitating electrodes with relatively narrower interspace of 1.5 $\mu$m have excellent gas-sensing characteristics to hydrogen concentration ranging from 2 to 1000 ppm at operating temperature of 120–275 °C.

Methods

The fabrication of In$_2$O$_3$ nanotower hydrogen sensors includes two parts. One is the preparation of comb-shaped interdigitating electrodes with relatively narrower interspace of 1.5 $\mu$m on the silicon substrate, and the
corresponding processes are basically the same with our previous works [4, 5].

Another part is the synthesis of In$_2$O$_3$ nanotowers on the silicon substrate by thermal evaporation of active carbon and In$_2$O$_3$ powders. The active carbon and In$_2$O$_3$ powders are mixed in a 1:1 weight ratio as the reaction source and put near the silicon substrate, which are placed inside the little quartz tube that is pulled into a large quartz tube in a horizontal tube electric furnace. After the whole system is evacuated by a vacuum pump for 20 min, the argon gas is guided into the system at 250 sccm and the pressure is kept at 350 Torr. Then, the system is rapidly heated up to 1050 °C at 40 °C/min from the room temperature and kept this temperature for 1 h. Finally, the system is cooled down to the room temperature for several hours by natural cooling. The In$_2$O$_3$ nanotowers are synthesized. Field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM) are used to identify the morphology and structure of the products.

After that, the In$_2$O$_3$ nanotowers are scraped down from the silicon substrate and ultrasonically dispersed in ethanol for 30 min to form a suspension. Then, the suspension is taken out by straw and sprinkled on the Cr comb-shaped interdigitating electrodes so as to constitute a gas sensor chip after the ethanol evaporation. The corresponding schematic diagram of the gas sensor chip is shown in Fig. 1a. The Schottky contact between the In$_2$O$_3$ nanotower and the Cr comb-shaped interdigitating electrode forms the Schottky diode. The corresponding temperature-dependent (25 – 240 °C) I-V measurements are performed by using two regulated DC power supplies (RICH/RS1303DQ) and a digital multimeter (VICTOR/VC890D).

The heater of the gas sensor and the corresponding schematic diagram are shown in Fig. 1b, c. The heater steel silks on the thermal insulation material are connected with the metal pins “1” and “4.” Each gas sensor chip is put on the heater steel silks and bonded to another two metal pins so as to constitute a sensor element. The sensor element and the corresponding schematic diagram are shown in Fig. 1d, e. When the heating voltage is applied to metal pins “1” and “4,” the temperature of the heater steel silks will rise up according to Joule’s law so as to make the temperature of gas sensor chip rise up. When the bias voltage is applied to metal pins “3” and “6,” the electrical signal measurement for the gas sensor can be carried out. The sensor temperature at different heating voltages is measured by contacting a thermocouple to the upper side of the gas sensor chip.

Each sensor element is packaged with a stainless steel mesh cap as shown in Fig. 1f. After that, the six metal pins of each sensor element are inserted in the corresponding holes of one measurement unit in the test gas chamber as shown in Fig. 1g. There are 10 measurement units in the test gas chamber, so 10 sensor elements can be tested at the same time. Then, the test gas chamber is sealed. By controlling gas-sensing characterization system (Gyjf Technology Co. Ltd., People’s Republic of China/JFO2E) consisting of gas mixer instrument, measurement instrument, and computer, certain concentration gas or air is passed into the test gas chamber based on a flow-through technique in different circumstances [6], and the corresponding schematic diagram is shown in Fig. 1h. In our case, the concentration of hydrogen gas is ranging from 2 to 1000 ppm. At the same time, bias voltage of 8.9 V is as working voltage, and certain heating voltage ranging from 3 to 5.1 V is as heating voltage which is supplied to test the gas chamber so as to apply to each tested sensor element. The resistance change of the gas sensor can be caught by the measurement instrument and displayed on the computer.

Results and Discussion

The characteristics results of the In$_2$O$_3$ nanotowers shown in Fig. 2 have been displayed in our previous work which is about the field emission properties of the In$_2$O$_3$ nanostructures [7]. The highly magnified FESEM image of the synthesized In$_2$O$_3$ nanotowers is shown in Fig. 2a. The four sides of the nanotower are chucked up with octahedrons one after another so that the nanotower possesses high surface-to-volume ratio property. The corresponding XRD pattern of samples in Fig. 2b shows that the fabricated nanostructures are indexed to the cubic In$_2$O$_3$. According to PDF No. 06-0416, the lattice constants of the cubic In$_2$O$_3$ are $a = 10.118$ Å, $b = 10.118$ Å, and $c = 11.118$ Å, respectively. Figure 2c is a typical TEM bright-field image of an individual In$_2$O$_3$ nanotower with an octahedral cap size of 600 nm. The HRTEM image shown in Fig. 2d is recorded at the body section of the In$_2$O$_3$ nanotower in Fig. 2c. The interplanar spacing of 0.715 nm is corresponding to the (011) crystallographic plane of cubic In$_2$O$_3$ lattice, and the corresponding selected area electronic diffraction (SAED) pattern in Fig. 2e recorded with an electron beam perpendicular to the surface of the In$_2$O$_3$ nanotower demonstrates that the In$_2$O$_3$ nanotower is single crystal and the growth direction is along [200].

The whole synthesis is conducted under the reducing atmosphere. So, the stoichiometric proportion of In and O has been further identified by quantitative x-ray photoelectron spectroscopy (XPS) analysis (in Fig. 3) performed on the product. A wide-scan XPS spectrum shown in Fig. 3a indicated that the product is consisted mainly of In and O. The contaminated carbon is attributed to a small amount of graphite from the reaction source. For its XPS spectrum of In 3d shown in Fig. 3b, because of the spin-
orbital splits, In $3d_{5/2}$ and In $3d_{3/2}$ have characteristic double peaks located at 444.96 and 453 eV, respectively, corresponding to the binding energy of In$^{3+}$ in In$_2$O$_3$ [8]. For its XPS spectrum of O1s shown in Fig. 3c, the O1s peaks can be divided into two peaks, centered at 530 eV (O1) and 532 eV (OII), respectively. The O1 sub peak is assigned to the lattice oxygen in the In$_2$O$_3$ nanotower [8–11], and the OII sub peak is usually associated with the chemisorbed oxygen ions in the oxygen vacancy ($V_o$) region [8, 10, 11]. The atomic ratio of O:In was 4.4:1, which did not agree with the stoichiometric proportion of O and In presenting in In$_2$O$_3$. Excrecent O may be adsorption oxygen [12]. As the area ratio of OI/OII is about 1/4.6, so the chemical formula of the nanotowers is In$_2$O$_{1.57}$, implying that a large amount of oxygen vacancies are introduced in the product.

Temperature-dependent $I$-$V$ plots for representative Cr/In$_2$O$_3$ nanotower Schottky diode before exposure to H$_2$ are shown in Fig. 4a. The primary conduction mechanism at Schottky diodes, in general, is due to the flow of majority charge carriers over the barrier by a thermionic process [13]. The electrical characterization of a
Schottky diode necessitates the determination of the barrier height and the ideality factor. For an ideal diode, the diode ideality factor should be nearly equal to unity. But in a real situation, it may increase when the effects of series resistance, leakage current, etc. come into play [13]. Depending on the temperature ($T$) and applied voltage ($V$), different transport mechanisms might be simultaneously operative in the Schottky diode and modulate the charge transport. Assuming that the thermionic emission is the most predominant mechanism, the general form of the temperature dependence of the current may be expressed as [13–15]:

$$I = AA^* \exp(-\beta \phi_B) \exp\left(\frac{\beta(V-IR)}{n}\right)$$  \hspace{1cm} (1)

where, $\phi_B$ is the effective barrier height, $A$ is the junction area, $A^*$ is the Richardson constant, $n$ is the ideality factor, $R$ is the series resistance, and $\beta = q/kT$. In such a case, the generalized Norde method can be used to evaluate the effective barrier height and diode ideality factor from $I$-$V$ measurements [13, 14]. The effective barrier height and ideality factor measured at different temperatures for Cr/In$_2$O$_3$ nanotower Schottky diode are shown in Fig. 4b. The barrier height can be seen to increase linearly with temperature. On the other hand, the ideality factor for the Schottky diode decreases from 2.93 to 0.82 with an increase in temperature. Deviation of the ideality factor from unity may be due to the existence of high series resistance [14].

$\text{H}_2$ sensing characteristics are investigated when the sensor are exposed to different $\text{H}_2$ concentrations ranging from 2 to 1000 ppm. The different heating voltages of 3, 3.5, 4, 4.5, and 5.1 V correspond to the different substrate temperatures of 120, 160, 200, 240, and 275 °C, respectively. The measurement time is 3500 s in the whole test process. Sensor resistances decrease abruptly upon exposure to $\text{H}_2$ and recover to initial values after purging by dry air. After several circles between the test gas and dry air, the In$_2$O$_3$ nanotowers sensor can still recover to the initial states, indicating good reversibility. The responses of the sensor are shown in Fig. 5a. We calculated
Fig. 3  
(a) Wide-scan XPS spectrum of the In$_2$O$_3$ nanotowers.  
(b) Its spectrum of In 3d.  
(c) Its spectrum of O 1s.
the response of the sensor using the expression of Response\% = \left( R_o - R_g \right) / R_o \times 100\% \ [16]. Here, R_o and R_g are the resistance of the sensor before and after exposure to the tested gas, respectively. Figure 5b shows the response as a function of operating temperatures from 120 to 275 °C for the sensor exposed to different H\textsubscript{2} concentrations of 2–1000 ppm. In\textsubscript{2}O\textsubscript{3} nanotower gas sensor reaches the maximum response value of 83 \% at an optimal operating temperature of 240 °C.

During exposure to increasing H\textsubscript{2} concentrations ranging from 2 to 1000 ppm under the optimal operating temperature of 240 °C, the steady-state resistance response of the sensor is also investigated and shown in Fig. 6a. According to the Zhu et al. [16], this should be done in a stable environment, and the time of measurement should be longer enough to insure adsorption of hydrogen molecules to reach a steady state. Figure 6b shows that the corresponding steady-state conductance
The response time of the sensor follows a power law depending on the H₂ gas concentration, \( G_{\text{gas}} = G_{\text{air}} + \alpha \text{(concentration)}^\beta \), where \( \alpha \) is a constant, \( \beta \) is a power exponent, and the ideal value is 0.5 [17]. The experimental data deduced from the measurement results in Fig. 6a is well consistent with the exponent fitting results, and the corresponding values of \( \alpha \), \( \beta \), and correlation coefficient \( R \) obtained in the process of fitting are indicated in Fig. 6b. For the \( \beta \) value of 0.48578, the small deviations from the ideal value of 0.5 probably relate to either agglomeration or zones in the structure that are less sensitive to H₂ than others, as modeled by Scott et al. [18].

Response time is also an important parameter for a gas sensor, which is defined here as the time reaching 90% of the final equilibrium value [19]. The corresponding response time of the sensor exposed to H₂ concentrations ranging from 2 to 1000 ppm at the operating temperature of 240 °C is indicated in Fig. 7a. With the hydrogen concentration increasing from 2 to 1000 ppm, the response time decreases from 127 to 63 s. To be sure, although interdigitating gap is smaller, the response time is relatively longer compared with that of the relevant report [20]. As for the reasons, we would like to elaborate on two aspects. Firstly, it is related with the longer path between the gas mixer instrument and the test gas chamber as shown in Fig. 1h. Secondly, the relatively larger size of our nanotowers compared with that of relevant report [20] results in a correspondingly less

\[ G = 1/R \]
surface-to-volume ratio, which can increase the response time too [20–22]. The time dependence of resistance of the In$_2$O$_3$ nanotowers on exposure to 500 ppm H$_2$ at different operating temperatures of 120–240 °C is shown in Fig. 7b. The rate of resistance change becomes greater as the temperature increases. The inset figure shows the rate of Arrhenius plot for the resistance change of nanostructures. An adsorption activation energy of 24.67 kJ/mol for the In$_2$O$_3$ nanotowers as shown in Fig. 7b is larger than that of 11.8 kJ/mol for the Pd-coated ZnO nanowires [23], that of 2.2 kcal/mol for the Pd-coated GaN nanowires [24], and that of 23.6 kJ/mol for the Pt-coated W$_{18}$O$_{49}$ nanowire networks [16].

Selectivity of the gas sensor is very important in the gas-sensing application. As we know, In$_2$O$_3$ is one kind of broad-spectrum sensitive material. The selective property is tested by exposing the sensor in reducing gases such as CH$_4$, C$_3$H$_8$, C$_2$H$_2$, CO, C$_2$H$_5$OH, and H$_2$, respectively, which is shown in Fig. 8a. The concentration values are 10, 100, and 1000 ppm, and the operating temperatures are 120 and 240 °C. It is very clear to discover that the sensor exhibits much higher responses to H$_2$ in comparison to that of CH$_4$, C$_3$H$_8$, and C$_2$H$_2$, respectively, which is due to the reason that the hydrogen with the smallest molecular size can easily pass through the surface dense layer and react intensely with the negatively charged...
Fig. 7  

(a) One cycle of H₂ in and out in the concentration range of 2–1000 ppm under an optimal operating temperature of 240 °C for the sensor.

(b) Resistance vs. time on exposure to 500 ppm of H₂ under different operating temperatures of 120–240 °C from the sensor, the inset figures showing the corresponding Arrhenius plot based on the rates of change of the resistance.

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oxygen adsorbates on the In$_2$O$_3$ surface [20]. However, the sensor exhibits slightly higher responses to H$_2$ than that of CO and C$_2$H$_5$OH, respectively, which is largely related with the activation energy of CO and C$_2$H$_5$OH being close to hydrogen. So, further study should be focused on improving the selectivity of the In$_2$O$_3$ nanotower gas sensors through surface modification with noble metals (Pt, Pd, Au, etc.). In addition, temperature modulation is also another efficient method for improving the selectivity of the metal oxide gas sensors [25].

In order to improve the selectivity of the sensor to the macromolecular gas such as CO or C$_2$H$_5$OH, we take an effective method to install the activated carbon or zeolites on the cover of the sensors.

The long-term stability of the sensor is also displayed in Fig. 8b. We measure the response of the sensor to 1000 ppm H$_2$ at an operating temperature of 240 °C every 3 days. Clearly, the sensor shows relatively stable response in 30 days.

Hydrogen-sensing response of the In$_2$O$_3$ nanotower gas sensor operated at 240 °C in comparison to those of the reported sensors using In$_2$O$_3$-based nano- or micro-

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**Fig. 8** a The selectivity properties of the sensor to reducing gases such as CH$_4$, C$_2$H$_6$, C$_3$H$_8$, CO, C$_2$H$_5$OH, and H$_2$, at the concentration of 10, 100, and 1000 ppm and under the different operating temperatures of 120 and 240 °C. b Long-term stability of the sensor to 1000 ppm H$_2$ at the operating temperature of 240 °C in 30 days.
structured materials is shown in Table 1. The range of the Response% of all the sensors normalized to \((R_o - R_g)/R_o*100\%\) is from 0 to 100 % due to \(R_g\) smaller than \(R_o\) and greater than 0. Thus, these results definitely show that the \(\text{In}_2\text{O}_3\) nanotower hydrogen sensor has basically achieved better responses than those of the reported sensors [3, 26–38].

The growth mechanism of the \(\text{In}_2\text{O}_3\) nanotowers can be described to be the VS process, and the corresponding schematic illustration is shown in Fig. 9a. It is well-known that the growth rate perpendicular to different planes is proportional to their surface energies. For \(\text{In}_2\text{O}_3\) with a bcc structure, the surface energy relationships among three low-index crystallographic planes should correspond to \(\gamma_{[111]} < \gamma_{[100]} < \gamma_{[110]}\) [39]. The shape of the pyramid tip is consistent with the cubic crystal structure of \(\text{In}_2\text{O}_3\) [40]. In the \(\text{In}_2\text{O}_3\) cubic structure, the \{001\} family planes contain the three equivalent planes (100), (010), and (001), which are perpendicular to the three directions [100], [010], and [001], respectively. Pyramids bounded by [111] facets with the highest (111) to that of (100) surface energy ratio possess the lowest surface energy [40]. The difference of surface energies among [110], [100], and [111] facets can lead to their different growth rates, and the growth rates of three growth directions have such relationships: \(\gamma_{[111]} < \gamma_{[100]} < \gamma_{[110]}\) [39]. As shown in the inset figure in Fig. 9a, after the 0-D growth, the (110) plane will disappear earlier, and the (111) plane will be preserved [39]. At the initial stage of heating, the indium vapor gradually evaporates out of the \(\text{In}_2\text{O}_3\) through a carbothermal reduction reaction, so the saturation ratio is low at this stage. Under a low saturation ratio, the 0-D nucleation and growth begin, and an octahedron forms under a VS mechanism [39], which is shown in the first process. According to a self-catalyzed effect, the surface polarity of the (111) plane of the cubic lattice in \(\text{In}_2\text{O}_3\) octahedron can depress the relatively high nucleation potential barrier of \(\text{In}_2\text{O}_3\) at the low temperature and induce the \(\text{In}_2\text{O}_3\) nucleation on the plane [41]. Therefore, the four little 0-D \(\text{In}_2\text{O}_3\) octahedrons can be formed at the four (111) plane of the big \(\text{In}_2\text{O}_3\) octahedron, which is shown in the second process. During the 0-D growth, the indium vapor is uninterruptedly evaporated, so the saturation ratio gradually increases and finally reaches the critical value of the 1-D growth. Then, the 1-D growth at the top plane of the four little 0-D \(\text{In}_2\text{O}_3\) octahedrons along the [001] direction begins. The 1-D growth consumes abundant reagent species and results in a decrease in the saturation ratio, so the 1-D growth stops and new 0-D growth begins. The 0-D growth will make the newly formed four little octahedral configurations. During the 0-D growth, the saturation ratio increases, and a new round of 1-D growth begins [39]. After the alternating 0-D and 1-D growths, the body of tower-shaped nanostructure continuously grows out, which is shown in the third process. As the reaction between the \(\text{In}_2\text{O}_3\) powders and the active carbon from the initial stage develops, the reagent’s vapor pressure turns bigger and bigger. The continuously increasing

| Type                  | Operated temperature (°C) | Response% (\(\Delta R/R_o*100\%\)) toward \(H_2\) under the following concentrations (ppm) |
|----------------------|--------------------------|---------------------------------------------------------------------------------------------|
| \(\text{In}_2\text{O}_3\) nanotowers | 240                      | 13 21 50 64 83                                                                             |
| \(\text{In}_2\text{O}_3\) nanowires [3] | 400                      | 17 60                                                                                      |
| \(\text{In}_2\text{O}_3\) nanoneedles [3] | 350                      | 10.7 20                                                                                   |
| \(\text{ZnO/In}_2\text{O}_3\) nanorods [26] | 20–25                    | 9.8 15.5 20.5                                                                             |
| \(\text{In}_2\text{O}_3\) thin films [27] | 50                       | 6.5                                                                                        |
| \(\text{In}_2\text{O}_3\) nanowires [28] | 200                      | 10                                                                                         |
| \(\text{Au-loaded In}_2\text{O}_3\) nanofibers [29] | 140                      | 33                                                                                         |
| \(\text{In}_2\text{O}_3\) hollow nanospheres [30] | 300                      | 41                                                                                         |
| \(\text{In}_2\text{O}_3\) nanowires [31] | 300                      | 69                                                                                         |
| \(\text{In}_2\text{O}_3/ZnO\) nanowires [32] | 400                      | 83                                                                                         |
| \(\text{In}_2\text{O}_3\) nanowires [32] | 300                      | 71                                                                                         |
| \(\text{In}_2\text{O}_3\) flower-like microspheres [33] | 150                      | 10                                                                                         |
| \(\text{In}_2\text{O}_3\) urchin-like microspheres [34] | 150                      | 10                                                                                         |
| \(\text{In}_2\text{O}_3/La/Pd}\) [35] | 100                      | 3                                                                                          |
| \(\text{In}_2\text{O}_3\) nanofibers [36] | 300                      | 43                                                                                         |
| \(\text{In}_2\text{O}_3\) nanowires [37] | 250                      | 17.9                                                                                       |
| \(\text{In}_2\text{O}_3\)Se [38] | –                        | 40                                                                                         |
reagent’s vapor pressure will continuously lead to large lateral and small axial growth rates, which will induce to the formation of 1-D structure with continuously increased size [42]. Therefore, the size of the In$_2$O$_3$ nanotowers can be continuously increased from top to bottom as shown in the fourth process.

The unique hydrogen-sensing properties based on the In$_2$O$_3$ nanotower can be explained as follows. In the open air, the chemisorbed oxygen ions (O$_2$ or O$^-$) form on the surface of the In$_2$O$_3$ nanotowers leading to a depletion region in surface layer owing to the electron shift from In$_2$O$_3$ to oxygen. When the hydrogen is injected, H$_2$ reacts with chemisorbed oxygen ions, which releases electrons back to the surface of the In$_2$O$_3$ nanotowers and alter its electrical conductivity of the structures. According to the XPS spectrum of O1s shown in Fig. 3c, it appears that a high concentration of chemisorbed oxygen ions will favor the forward reaction [2]. For example, it is found that the ethanol-sensing responses of In$_2$O$_3$ increase with the increasing intensity of chemisorbed oxygen [9]. In addition, because of the response of the metal oxide sensor to methanol depending on

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**Fig. 9**  
(a) The growth mechanism of the In$_2$O$_3$ nanotower, the inset figure is the schematic illustration of 0-D growth with octahedral configuration under the VS mechanism [39].  
(b) The Cr/In$_2$O$_3$ Schottky junction and (c) the corresponding energy-level diagram.  
(d) The contact between two In$_2$O$_3$ nanotowers and (e) the corresponding energy-level diagram.
the basicity of the metal oxide [43] and the basicity controlled by the electronic density which is generated from the $V_o$ [9], the hydrogen-sensing properties of the In$_2$O$_3$ nanotowers are excellent due to lots of $V_o$ being introduced in the In$_2$O$_3$ nanotowers in this paper.

The hydrogen-sensing mechanism of the sensors is attributed to not only the hydrogen-sensing properties based on the In$_2$O$_3$ nanotower discussed above but also the structure characteristics of the sensors as schematically shown in Fig. 9b–e. Besides the change of the Schottky barrier height in the Cr/In$_2$O$_3$ Schottky junction as shown in Fig. 9b, e, the thermoelectronic emission due to the contact between two In$_2$O$_3$ nanotowers as shown in Fig. 9d, e will contribute for the hydrogen-sensing mechanism too.

The electrical response comes from the variation of the Schottky barrier height and barrier width as a result of adsorption of gaseous species at the Schottky contact. The response due to adsorption can be explained from the band diagram at the metal/nanostructure contact. After the exposure to H$_2$, Cr adsorbs H$_2$ by catalytic chemical adsorption, which reduces the Schottky barrier height [14]. The catalytic effect of chromium can be understood in two ways [44]. The first one is related to the work function value of the chromium which leads to an excess of free bonds near the surface region, then producing an important oxidation which favors the subsequent reactions with the H$_2$. The second one is related to the formation of a Cr$_2$O$_3$ phase close to the surface region, which increases the catalytic activity of this region due to the fact that the surface chromium atoms can be easily oxidized and reach an effective valence of four. So, they can adsorb a complete monolayer of active oxygen.

In an individual In$_2$O$_3$ nanotower, free carriers (electrons) can transport along the conduction channel. But when transporting between two contacting In$_2$O$_3$ nanotowers, the electrons have to pass through a potential barrier at the junctions and a thermoelectronic emission mechanism can be used to describe the electron transportation in the junctions [16]. The change in resistance during the adsorption or desorption process of H$_2$ species is likely to be caused by the alteration both in the width of the surface depletion layer of each In$_2$O$_3$ nanotower and in the height of potential barriers built at the contacted junctions between two In$_2$O$_3$ nanotowers. These two-fold effects may facilitate less response time and higher response to certain chemical species [45].

**Conclusions**

In summary, we report that new In$_2$O$_3$ nanotowers synthesized via thermal evaporation and distributed on Cr comb-shaped interdigitating electrodes with relatively narrower inter-space of 1.5 μm have high response, fine long-term stability, and small deviation from ideal value of power exponent $\beta$, in the hydrogen concentration ranging from 2 to 1000 ppm and at the operating temperature of 120–275 °C. The Schottky contact between the In$_2$O$_3$ nanotower and the Cr comb-shaped interdigitating electrode forms the Cr/In$_2$O$_3$ nanotower Schottky diode, and the corresponding temperature-dependent $I$-$V$ characteristics have been measured. The diode exhibits a low Schottky barrier height of 0.45 eV and ideality factor of 2.93 at room temperature. The growth mechanism of the In$_2$O$_3$ nanotowers has been discussed in detail, which is account for the high surface-to-volume ratio of the morphology. Lots of oxygen vacancies and chemisorbed oxygen ions exist in the In$_2$O$_3$ nanotowers according to the XPS results. The change of Schottky barrier height in the Cr/In$_2$O$_3$ Schottky junction and the thermoelectronic emission due to the contact between two In$_2$O$_3$ nanotowers mainly contribute for the H$_2$ sensing mechanism. The In$_2$O$_3$ nanotowers hydrogen sensors are promising for further practical applications.

**Competing Interests**

The authors declare that they have no competing interests.

**Authors’ Contributions**

ZQZ carried out all the experimental processes, characterization, and mechanism research. LFZ conceived the study and participated in its coordination. BW drafted the manuscript. All authors read and approved the final manuscript.

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