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In/Pd-Doped SnO₂-Based CO Micro-Structure Sensor with High Sensitivity and Quick Response *

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In/Pd-doped SnO₂ is synthesized via a sol-gel method and coated on a silicon substrate with Pt electrodes to fabricate a micro-structure sensor. The sensor can be used to detect CO down to 1 ppm (the sensitivity is about 3), and the response time and recovery time are about 5 and 15 s, respectively. Excellent selectivity is also found based on our sensor. These results demonstrate a promising approach to fabricate high-performance CO sensors with high sensitivity and quick response.

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Sensors to detect toxic and flammable gases have gained special focus driven by their diverse applications in air-quality detection, inflammable-gas inspection, environmental monitoring, healthcare and security, and so on.^[1–13] Among toxic and flammable gases, carbon monoxide (CO) is the most interesting for study. CO is a kind of colorless, tasteless, widespread and toxic gas. Even at low concentrations, well below immediately dangerous to life and health (IDLH) levels, it has negative effects on human health. It is represented that this highly toxic gas can attach to the haemoglobin, which damages the human body by producing a reduction in cellular respiration.^[14] Therefore, it is becoming an urgent subject to accurately and quickly detect CO gas in atmosphere air.

SnO₂ is one of the most promising metal oxide semiconductors for CO sensor applications, and the development of SnO₂ sensors to CO has been the focus of numerous research works in the world.^[14] Extensive studies have been put on improving the sensing performance based on the SnO₂-based CO sensors, such as adding catalysts, doping metals and metal oxides, decreasing grain size, controlling pore and optimizing fabrication process, etc. However, most of these sensors are fabricated by coating the sensing materials on the outerface of the ceramic tube with electrodes and heaters. They are hard to keep consistency and homogeneity, and also difficult to integrate with other devices.

In this study, we synthesize In/Pd-doped SnO₂ through a sol-gel method, and fabricate a micro-structure sensor by screen-printing the as-synthesized SnO₂ on a silicon substrate with Pt heater and signal electrodes. Excellent sensing properties such as high sensitivity, quick response and good selectivity are ob-

served at 140°C. These results make our sensor a good candidate in practical CO sensors.

In/Pd-doped SnO₂ was prepared through a sol-gel method using SnCl₄ · 5H₂O, citric acid, InCl₃, PdCl₂, and deionized water as precursors. In a typical synthesis process, SnCl₄ · 5H₂O (5 g) was added to an aqueous solution consisting of citric acid (0.5 g) and deionized water (100 mL). After dissolving deeply, aqueous ammonia (0.5 M) was added as a precipitator under strong stirring until the pH of the solution reached 3 to obtain Sn(OH)₄ precipitation. Then the resultant product was centrifuged, and the solid fraction was washed with deionized water. This cycle was repeated for several times in order to eliminate the chloride ions. The precipitate was dried under an infrared lamp, and then ground using an agate pestle and mortar to obtain Sn(OH)₄ powder. In/Pd-doped SnO₂ was obtained by mixing InCl₃ · 4H₂O (22 mg), PdCl₂ (5 mg) and as-synthesized Sn(OH)₄ (250 mg), grinding in an agate mortar for 2 h, finally calcining at 650°C for 2 h in air. The crystal structures and morphologies of the sample were examined by x-ray diffraction between 20° and 80° in 2θ (XRD, Rigaku D/max-Ra with Cu Kα, λ = 0.15418 nm) and field emission scanning electron microscopy (FE-SEM, JEOL JEM-6700F microscope operating at 5.0 kV).

The structure of the micro-structure sensor is shown in Fig. 1(a). The ⟨100⟩ crystal orientational monocrystalline silicon is chosen to be the substrate. SiO₂ is chosen as the insulating layer owing electronic isolation properties. Its heat conductivity is far less than that of Si, which can heat the sensing materials efficiently. The interdigitated signal and the heater electrodes are made of Pt due to its high stability at high temperature. The sensing material is designed to be screen-printed on the top surface of the substrate

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directly, which can greatly improve the heat conducting efficiency. The design of the heater and signal electrodes are shown in Fig. 1(b). The continuous red stripes are Pt heater electrodes, while the yellow stripes are signal electrodes. The width of heater electrodes, signal electrodes and spaces are 50 μm , 50 μm , and 25 μm , respectively. The total size of the sensors is $2 \times 1 \times 0.3 \text{ mm}^3$.

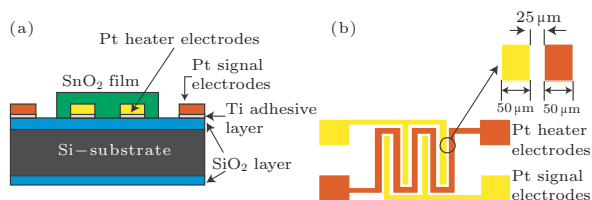


Fig. 1. (a) Cross section of the micro-structure sensor, and (b) design of Pt heater and signal electrodes.

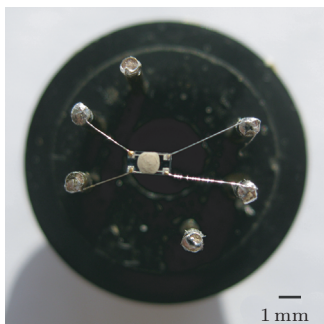


Fig. 2. Photograph of the micro-structure gas sensor on the socket.

The fabrication of the micro-structure sensor was achieved according to the following steps: (a) growing SiO_2 (thickness of 3000 \AA) on the Si-substrate as insulating layer, (b) sputtering titanium (thickness of 200 \AA) as an adhesive layer, (c) sputtering platinum (thickness of 1800 \AA) as metal electrodes, (d) mask patterns transfer to the Si wafer by photolithography, (e) etching the two layer metals (Ti and Pt), (f) removing the photoresist, (g) finally screen-printing In/Pd-doped SnO_2 (thickness of 100 μm) on the substrates. Figure 2 is a photograph of the micro-structure sensor on the socket.

Gas sensing properties were measured using a static test system. Saturated target vapor was injected into a glass test chamber (20 L in volume) by a syringe through a rubber plug. After being fully mixed with air (relative humidity was about 25%), the sensor was put into the test chamber. When the sensitivity reached a constant value, the sensor was taken out to recover in air. The electrical properties of the sensor were measured by the CGS-1 intelligent test system (Beijing Elite Tech Co. Ltd., China).

The sensitivity of the gas sensor in this study is defined as

$$R = R_a/R_g, \quad (1)$$

where R_a is the baseline resistance of the sensing film

in pure air (without access to a target gas) and R_g represents the resistance in a target gas environment. The time taken by the sensor to achieve 90% of the total resistance change is defined as the response time in the case of adsorption or the recovery time in the case of desorption.

Figure 3(a) shows the XRD pattern of In/Pd-doped SnO_2 . All the prominent peaks in the pattern correspond to the rutile structure of SnO_2 and are indexed on the basis of JCPDS file No 41-1445.^[15] No peaks corresponding to the doping materials are observed, suggesting that In and Pd get incorporated into the tin oxide lattice. The particle size of In/Pd-doped SnO_2 is estimated using FE-SEM, as shown in Fig. 3(b). The average diameter of In/Pd-doped SnO_2 is about 10 nm.

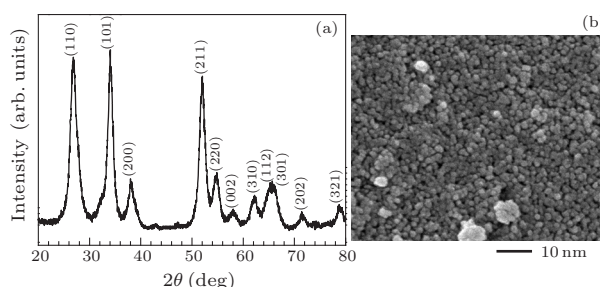


Fig. 3. (a) XRD pattern and (b) FE-SEM image of In/Pd-doped SnO_2 .

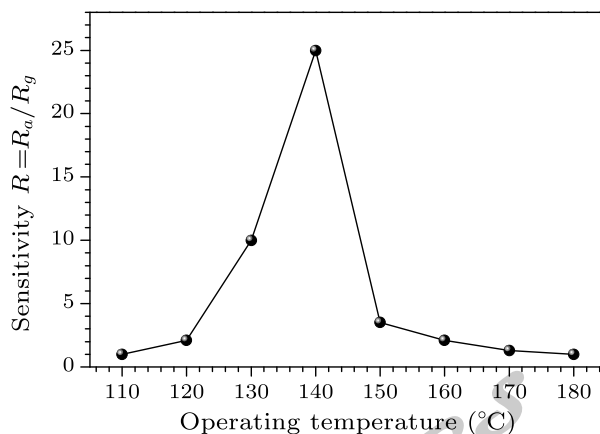


Fig. 4. Sensitivity of the micro-structure sensor to 50 ppm CO at different temperatures.

Gas sensing experiments were performed at different temperatures in order to find out the optimum operating temperature for CO detection. Before exposing to the target gas, the sensor was stabilized for 2 h at the working temperature. As can be seen in Fig. 4, the sensitivity increases and reaches its maximum at 140°C, and then decreases rapidly with the increasing temperature. Thus the optimal operating temperature is 140°C, and all the measurements were performed under this condition. The operating temperature of our sensor is measured by using the temperature measurement based on radialization power.^[16]

R_a of the sensor is measured to be about 13 M Ω . It is well known that response and recovery characters are important characteristics for evaluating the performances of gas sensors. The sensor responses to 1, 5, 20, 50, 100, and 200 ppm CO at 140°C are shown in Fig. 5(a). The signals from the sensor become stable within 5 s after it is exposed to CO, and return to the original values within 15 s after the tested vapor is replaced with air. Thus the response and recovery times of the sensor are about 5 and 15 s, respectively. Moreover, good repeatability has also been realized among the four cycles (Fig. 5(b)), which demonstrates the chemical stability of the sensor.

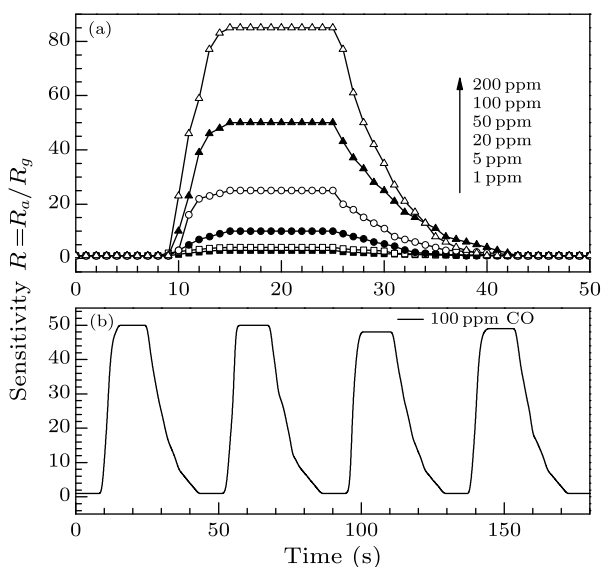


Fig. 5. Response and recovery of the micro-structure sensor to (a) different concentrations of CO and (b) 100 ppm CO for four cycles.

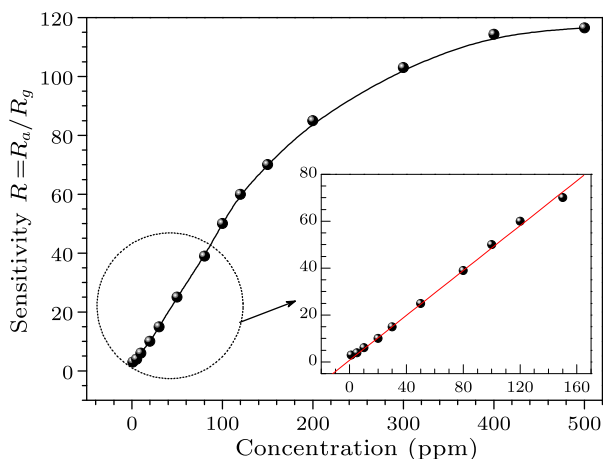


Fig. 6. Sensitivity of the micro-structure sensor vs. CO concentration, the insert is the calibration curve in the range of 1–150 ppm.

Figure 6 shows the sensitivity versus CO concentration of our sensor. It can be seen that the CO concentration as small as 1 ppm can be easily detected ($R_a/R_g = 3$). When the concentration increases to

5 ppm, the sensitivity turns to 4. The sensitivity of the sensor to 10, 20, 30, 50, 80, 100, 120, 150, 200, 300, 400, and 500 ppm CO is about 5, 10, 15, 25, 39, 50, 60, 70, 85, 103, 114, and 117, respectively. In fact, the sensitivity of a semiconducting oxide gas sensor can usually be empirically represented as $S_g = AP_g^\beta$, where P_g is the target gas partial pressure, which is in direct proportion to its concentration, and the sensitivity is characterized by the prefactor A and exponent β . Here β may have some rational fraction value (usually 1 or 1/2), depending on the charge of the surface species and the stoichiometry of the elementary reactions on the surface.^[17] As shown in the insert of Fig. 6, when CO concentration is in the range of 1–150 ppm, β is found to be 1. These results further confirm that our sensor can be used as a potential gas sensor with highly performance.

The selectivity of the sensor was tested by exposing the sensor to 50 ppm potential interference gases as shown in Fig. 7. This figure clearly shows that the sensor exhibits considerably lower sensitivities to other gases than that to CO. This high degree of selectivity coupled with high sensitivity make our sensor particularly interesting for CO monitoring applications.

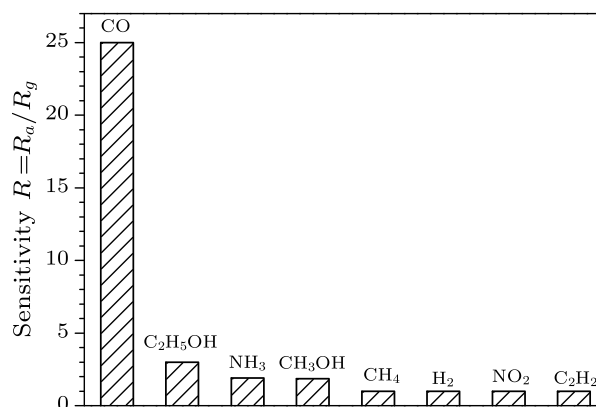
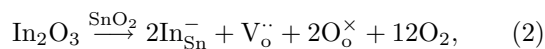


Fig. 7. Selectivity of the micro-structure sensors.

A possible mechanism for CO sensing in the present study is depicted as follows. It is well known that the change in resistance of semiconducting oxide gas sensors is primarily caused by adsorption and desorption of gas molecules on the surface of the sensing film.^[18] When sensors are surrounded by air, oxygen molecules will adsorb on the SnO₂ surface to generate chemisorbed oxygen species (O_2^- , O^{2-} , O^-), and thus SnO₂ will show a high resistance. When SnO₂ is introduced at moderate temperature of heating, SnO₂ is exposed to the traces of reductive gas. By reacting with the oxygen species on the SnO₂ surface, the reductive CO will reduce the concentration of oxygen species on the SnO₂ surface and thus increase the electron concentration, which eventually increases the conductivity of the In/Pd-doped sensors. The effect of In doping on the CO sensing properties of our sensor

may describe as fellow.^[19]

Since trivalent In^{3+} acts as an acceptor impurity, the replacement of Sn^{4+} by In^{3+} ions could be expressed as



where In_{Sn}^- represents In substitution in Sn sites, $\text{V}_{\text{O}}^{\cdot\cdot}$ represents lattice oxygen vacancies and $\text{O}_{\text{O}}^{\times}$ represents interstitial oxygen. This action could enhance the active surface states for the adsorption of detecting gases and eventually improve gas sensing properties.

The addition of Pd to sensor elements has been widely reported owning promotions of gas sensitivity and response rate.^[20] However, the exact way in which the dopant influences the sensing properties is still a subject of debate. Basically, two different mechanisms, that is, electronic and chemical sensitization, have repeatedly been applied. Many authors believe that Pd is a typical element of electronic sensitization.^[21] It is considered that Pd can form a stable oxide (PdO) in air, which is easily reduced to metallic Pd with a reducing gas. PdO produces a strongly electron-depleted space charge layer inside the semiconductor, while the electronic interaction is ruptured when it is reduced to metallic Pd. Therefore, the excellent CO sensing properties of In/Pd-doped SnO_2 sensor are ascribed to the cooperative effect of all the above-mentioned factors.

In conclusion, a micro-structure sensor has been fabricated from In/Pd-doped SnO_2 . The sensor with high selectivity can be used to detect CO down to 1 ppm (the corresponding sensitivity is 3). The response and recovery times are about 5 and 15 s, respectively. The results demonstrate that our sensor is a potential candidate for a high-performance gas sensor.

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