In Situ Localized Growth of Porous Tin Oxide Films on Low Power Microheater Platform for Low Temperature CO Detection

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Supporting Information

ABSTRACT: This paper reports a facile method for creating a nanostructured metal oxide film on a low power microheater sensor platform and the direct realization of this structure as a gas sensor. By fast annealing the deposited liquid precursors with the microheater, a highly porous, nanocrystalline metal oxide film can be generated in situ and locally on the sensor platform. With only minimal processing, a high performance, miniaturized gas sensor is ready for use. A carbon monoxide sensor using the in situ synthesized porous tin oxide (SnO2) film is made as a demonstration of this technique. The sensor exhibits a low detection limit and fast response and recovery time at a low operating temperature. This facile fabrication method is highly flexible and has great potential for large-scale gas sensor fabrication.

KEYWORDS: gas sensors, in situ synthesis, low power, microheater, nanocrystalline tin oxide, CO sensor

Solid-state chemical sensors have received considerable attention in recent years, in particular, for monitoring environmental pollution and air quality.1–5 Semiconducting metal oxide sensors are among the most promising solid-state chemical sensors due to the large variety of metal oxides available and their low cost in mass production.4–6 However, in order to obtain appropriate sensitivity levels, the metal oxides need to be heated to high temperature (∼300–500 °C), resulting in high power consumption (typically several hundred mW) and thus impeding their implementation as long-term, battery-powered gas monitors.6–8 Power consumption can be decreased by reducing the sensor size and/or the operation sensing temperature. Metal oxide gas sensor miniaturization can be accomplished through the use of microfabrication methods to create a microheater platform.9–11 Microheaters allow for high sensing temperatures to be reached with low input power through the use of a small heater element thermally isolated from the substrate. However, the shrunken device footprint means a loss of area for the sensing material, which negatively impacts sensitivity and lifetime. Nanostructured materials with high surface-to-volume ratios can improve the sensitivity through an increase in surface area per device footprint as well as a greater number of grain contacts in the conductive path, which amplify the signal during gas exposure.7

Nanostructured metal oxides have been shown to have better gas sensing performance than the corresponding bulk material.7 However, the integration of networks of nanowires or nanoparticles onto a microfabricated platform is difficult to control. Nanomaterial aggregation during film formation and sensor operation leads to a loss of active surface area and slows the diffusion of the target gas to the active sites.14,15 Formation of nanostructured films through the use of sacrificial templates such as polystyrene spheres,14,15 carbon nanotubes,16 or anodized aluminum oxides18 adds complexity and cost. There remains a need for a simple, effective approach to the preparation of nanostructured metal oxide films for low power, miniaturized gas sensors. In this letter, we present a strategy for the fabrication of high performance, miniaturized gas sensors through on-chip generation of highly porous and nanostructured metal oxide
films. Tin oxide, the most widely investigated metal oxide sensor material, is taken as the example to demonstrate the validity of this strategy. Taking advantage of the fast thermal response of the microheater platform, a liquid precursor is drop-cast onto the microheater and rapidly sintered to form a porous film of SnO₂ nanoparticles, which gives high surface area and allows for fast gas diffusion to all active sites. The exceptional gas sensing performance of the nanostructured SnO₂ film is demonstrated with fast, highly sensitive response to carbon monoxide at low operating temperature.

The microsensor consists of a porous nanostructured SnO₂ layer contacted by platinum electrodes deposited on a polycrystalline silicon (polysilicon) microheater embedded in a thin low-stress silicon nitride (LSN) membrane as illustrated in the cross-sectional schematic in Figure 1a. Figure 1b shows a real color optical image of the 3.5 × 3.5 mm² chip containing four microheater sensors. Full fabrication details can be found in ref 11. Figure 1c shows a zoomed-in view of a single microheater device with a heated area of only 50 × 50 μm², which results in a low power consumption (~18 mW to reach 500 °C). The sensing electrodes have a gap of only a few μm over the hottest region of the microheater, such that the sensor resistance is dominated by the metal oxide at this precise spot. Besides the low power consumption, other benefits of the microheater platform include the fast thermal response time (<100 μs),12 and excellent stability in the temperature range of interest (200–450 °C).11,12 Additionally, the closed membrane configuration makes deposition of sensing material from a liquid precursor much easier compared to bridge microheater structures.

The liquid SnO₂ precursor is prepared by mixing SnCl₄, NH₄OH, ethanol, and water under continuous stirring at room temperature. After stirring for 1 h, a 1 μL drop is placed on the packaged microheater chip (Figure S1) and the heater is powered to 85 °C for 10 min to evaporate the solvent. The addition of NH₄OH in the mixture helps form a gel-like phase19,20 that leads to a relatively smooth, uniform precursor film upon deposition and solvent evaporation, as seen in the scanning electron microscopy (SEM) image in Figure 2a. After the 10 min heating at 85 °C, the microheater temperature is ramped to 350 °C (12.5 mW) and held there for 2 h to form the final porous SnO₂ film. Because of the fast thermal response time of the microheater, the temperature reaches 350 °C in less than 1 ms, which leads to the quick removal of water from the gel-like precursor film to form a highly porous SnO₂ film. As widely explored in the fabrication of activated carbons, a fast heating rate leads to the formation of mesopores or macropores in the structure because of the rapid release of gaseous products.21–23

To understand the effect of heating rate, samples are prepared on silicon chips using an external hot plate. In the fast ramping case, the hot plate is preheated to 350 °C and the sample is placed on it after the 85 °C treatment. In the slow ramping case, the sample remains on the 85 °C hot plate and the temperature is changed to 350 °C, which is reached after several minutes. In Figure 2b, the slow heating rate film is very smooth, comparable to the precursor film in Figure 2a. On the other hand, SEM images of the SnO₂ film synthesized with the fast heating rate show more cracks and higher surface roughness (Figure 2c) than the precursor film and the slow heating rate film, confirming that the fast heating rate is the key to the porosity of the film. Increased film porosity in the sintered SnO₂ film is seen at several length scales from micron-sized cracks (Figure S2) to nanometer-sized pores (Figure 2e). The composition and phase purity of the sintered film are

Figure 2. SEM images of (a) smooth SnO₂ precursor film, (b) porous SnO₂ film formed with slow heating rate, and (c) SnO₂ film formed with fast heating rate. (d) XRD data confirming tetragonal rutile SnO₂ structure for porous SnO₂ film found in (c). (e) Low and (f) high magnification TEM images of porous SnO₂ film with small size interconnected nanoparticles. Inset: high resolution TEM indicating the lattice spacing of 0.336 nm, corresponding to (110) crystal structure of SnO₂.
examined by X-ray diffraction (XRD, Figure 2d), which confirms the conversion of the precursor to polycrystalline SnO₂.

The nanoscale features of the porous SnO₂ film are visible using transmission electron microscopy (TEM). In Figures 2e,f, interconnected nanoparticles with an average size of 4 nm are shown. Smaller particles have higher surface to volume ratios, which are favorable for gas sensing applications due to both the increased number of active sites per device footprint as well as the increased number of grain contacts in the conductive path. Numerous interparticle pores with diameters of 1–4 nm are uniformly distributed throughout the whole film. The inset of Figure 2f shows a lattice spacing of 0.336 nm, which can be readily indexed to the (110) crystal plane of the SnO₂ further confirming the formation of crystalline SnO₂. The corresponding selected area electron diffraction (SAED) pattern shown in Figure S3 also indicates the polycrystalline nature of the SnO₂. The SAED diffraction rings, plus the high background and broad peaks of the XRD, confirm the TEM observation of nanosized SnO₂ particles.

The porosity of the SnO₂ film on multiple length scales is expected to enhance gas sensing performance because it offers channels for gas diffusion to a large number of active sites. The porous features of the film are defined through the fast heating rate supplied by the microheater, making this a simple method to integrate a porous nanostructured sensing film onto a microheater-based sensor. Because the precursor solution is liquid, it is possible to manufacture these sensors with materials printing methods without concerns about stable suspensions of nanomaterials or clogged printer heads. Additionally, there is no concern about obtaining a connected network of nanomaterials between the sensing electrodes, as the liquid precursor is converted to the nanostructured metal oxide film precisely where required.

To demonstrate that the as-fabricated porous SnO₂ film is directly useful as a gas sensor, the detection of carbon monoxide is explored. Sensor measurement details can be found in Supporting Information. Figure 3a shows real-time resistance change of the SnO₂ sensor to various CO concentrations with a microheater operating temperature of 200 °C, which requires only 7 mW power consumption for continuous measurement. Operating the sensor at 200 °C represents an optimum for the sensitivity, response and recovery time, and power consumption (Figure S4 and Figure S5). As seen in Figure 3a, the sensor resistance shows rapid response during exposure to varied CO concentrations and full baseline recovery. Tin oxide is an n-type semiconductor and its resistance is determined by surface states, which are affected by the adsorption of oxygen species. In ambient air, chemisorbed oxygen species on SnO₂ surface trap electrons, creating an electron-depleted region, which leads to a barrier at the interface between contacting nanoparticles. The introduction of CO onto the surface at elevated temperature leads to reaction of CO with the surface oxygen species to form CO₂. The removal of the oxygen releases the trapped electrons and lowers the barrier between contacting nanoparticles, which leads to a decrease in resistance.

Figure 3b is a plot of the sensor response (Rair/Rgas) versus CO concentration, exhibiting a linear relationship, where Rair is the average sensor resistance in clean air and Rgas is the average sensor resistance during CO exposure once the response has stabilized. The sensitivity is comparable to earlier published work, but with a lower operating temperature (200 °C vs 300–500 °C), which allows for lower power consumption. The responses of three devices are within 20% of one another on average, demonstrating the uniformity of this process. Due to the accuracy of the mass flow controllers in the gas delivery system, the lowest concentration of CO that can be reliably delivered is 10 ppm (corresponding to signal-to-noise threshold of 17.4), but when using a typical signal-to-noise threshold of 3, the detection limit of the sensor is 1.75 ppm. The enhancement in gas-sensing properties of the porous SnO₂ sensor may be ascribed to the small crystalline size of the interconnected nanoparticles, which gives a high surface to volume ratio and generates more active sites per device footprint. Additionally, the small crystal size increases the number of grain contacts in the conductive path between sensing electrodes, increasing the number of energy barriers that are the main source of sensitivity. The average time to reach 90% of the stable sensor signal (t90) is 9 s and the t90 for recovery is 29 s. Other reported SnO₂-based sensors respond in several tens of seconds and take several minutes for recovery. The improved response may be attributed to the multiscale porosity, which allows for fast diffusion to all active sites. The nanostructured SnO₂ film shows excellent sensing performance, even with low operating temperature on a miniaturized microheater platform.

In summary, we have presented a flexible and facile route for the localized growth of porous metal oxide films on a microheater platform to obtain high performance gas sensors. By sintering the suitable liquid-phase metal oxide precursor with a fast heating rate, a nanostructured metal oxide film with multilength scale porosity can be generated right on the fabricated microheater platform. The demonstrated SnO₂-based CO sensor has low power consumption (~7 mW for 200 °C), low operating temperature (200 °C), low detection limit (~2 ppm of CO), fast response time (<10 s) and recovery time (<30 s), and high sensitivity. More importantly, this facile fabrication strategy provides a way to manufacture high performance sensors with other types of metal oxides, and has the potential for low cost mass production.
**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssen-sors.5b00302.

Microheater fabrication details, further material characterization, sensor testing, and measurement methods (PDF)

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**


(29) Yan, Q. G.; Liu, X. Y. Non-heating Room Temperature SnO2 Gas Sensors; In Chemical Sensors VI: Chemical and Biological Sensors


