Nanostructured Materials

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Metal Oxide "Nanosponges" as Chemical Sensors: Highly Sensitive Detection of Hydrogen with Nanosponge Titania**

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Semiconducting metal oxides are widely considered to be the most promising platform for solid-state gas sensors. As a result of enhanced responsiveness of conductance to surface effects in low-dimensional nanostructures, various forms of nanostructured metal oxides have been synthesized and their sensing properties studied.[1] In prior reports, metal oxides in the form of individual nanoscale belts,[2] rods,[3] tubes,[4] and wires[5,6] were synthesized by a number of techniques and showed encouraging gas-sensing properties. Recently, three-dimensionally (3D) interconnected nanostructures of metal oxides have attracted attention because of the promising performance of a prototype sensor.[7] Previously, we also developed a technological approach for fabricating patterned 3D nanoporous materials.[8,9] The 3D morphology is versatile, as it lends itself to large-scale production of highly sensitive sensors by leveraging on planar technologies, and could lead to development of low-cost and miniaturized sensing devices.

Herein, we demonstrate the use of 3D interconnected nanoscale walls and wires of nanosponge TiO_2 (NST) as ultrasensitive sensing elements for detecting H_2 gas with potential applications in fuel cells. Sensors based on NST exhibited the ultrahigh sensitivity of individual nanostructures. We used 3D TiO_2 (titania) in this study, as it has been widely investigated as a sensing material, and a wealth of data is available for comparison.

Arrays of NST pads were synthesized by wet oxidation followed by thermal annealing (see Experimental Section). The NST pad arrays fabricated were crack-free because the Ti pads were below the threshold value[9] (Figure 1a). The NST is spongelike and consists of interconnected nanowalls and nanowires (Figure 1b and c). Nanosponge TiO_2 formed from 500-nm-thick Ti films has a wire diameter or wall thickness of about 75 nm. However, NST morphology is dependent on Ti film thickness; NST formed from 150-nm films has smaller features. Wire diameter or wall thickness of NST formed from 150-nm-thick Ti films is about 40 nm. When Ti reacts with H_2O_2 solution, a hydrated gel layer is formed on the surface.[10] We believe that the concentration of Ti ions in the gel affects NST morphology. Average grain size of deposited Ti films increases with increasing film thickness. In thinner films, the concentration of Ti ions is higher owing to more pronounced grain-boundary diffusion. Higher concentrations of Ti ions result in denser gel layers and produce smaller pores and nanowire diameters, as well as thinner nanowalls.[11] The dependence of feature size on Ti ion concentration in the gel can be used to tailor NST morphology and properties.

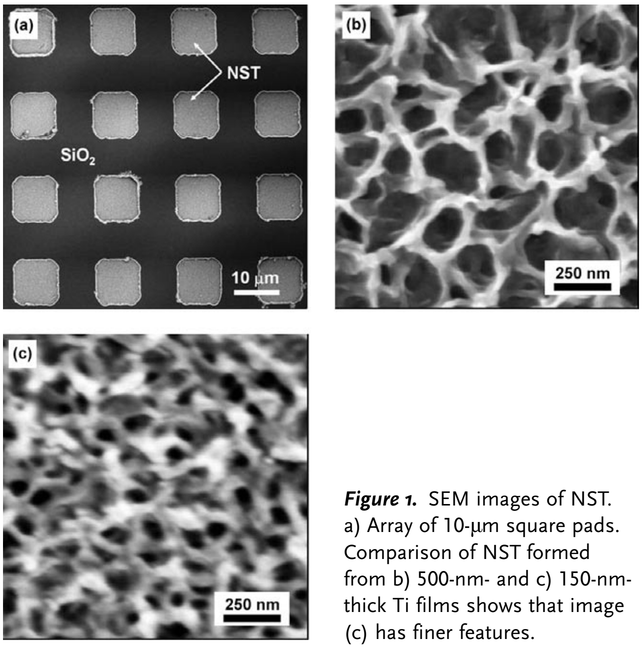

Figure 1. SEM images of NST. a) Array of 10-μm square pads. Comparison of NST formed from b) 500-nm- and c) 150-nm-thick Ti films shows that image (c) has finer features.

The crystal structure of NST was studied by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). A cross-sectional TEM image of an annealed NST layer formed from 500-nm-thick Ti film is shown in Figure 2a. The absence of cracks at the interface

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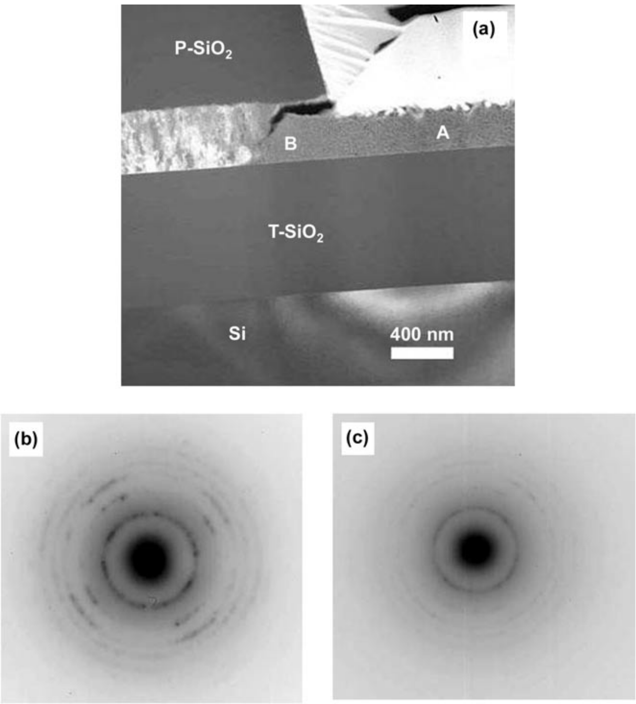

Figure 2. a) TEM cross-sectional image and SAED patterns at regions A (b) and B (c) labeled in image (a).

between NST and the underlying SiO_2 layer suggests good mechanical reliability of the sensing device. Indeed, cross-sectional TEM images of similar regions in devices that have undergone cyclic sensing tests do not reveal any cracks. The SAED patterns taken at center (region A) and periphery (region B) of pads are shown in Figure 2b and c, respectively. The more diffuse and less intense diffraction rings at the periphery of pads indicate that NST here is largely amorphous. This assertion was supported by electrical probing studies that revealed individual NST pads to be electrically isolated from each other. Amorphous titania has been reported to be electrically insulating.[4,12] The SAED patterns indicate that NST at the center of pads consists of the anatase phase of titania.[9]

Sensing devices were fabricated by depositing Ti/Pt on NST pads after thermal annealing (Figure 3). A sensing device with three NST pads connected in series and a close up view of one pad are shown in Figure 4a and b, respectively. Depending on application, pads can be metallized individually. In the following, we present results for sensing H_2 with a single 20-μm square NST pad formed from 500-nm-thick Ti film. The H_2 sensing capability of NST in vacuum and under atmospheric pressure was investigated.

The NST-based sensors are extremely sensitive to H_2 gas in vacuum. Figure 5 shows current–voltage (I–V) characteristics at 25 °C in the absence (I_0) and presence (I_{gas}) of H_2, as well as their difference ($I_{gas}-I_0$). Assuming H_2 is entrained as an ideal gas, the concentration of H_2 in the test chamber was calculated to be 1 ppm, which is near the lower concentration limit of our setup. As expected, current increased when H_2 gas was introduced, as it is a reducing gas and anatase is an n-type semiconductor. We believe that this minimum detection limit can be reduced further by increasing NST pad size or connecting pads in series.

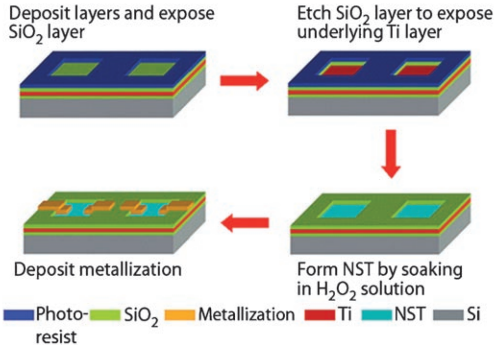

Figure 3. Schematic process flow sheet for fabrication of NST pad arrays and sensing device.

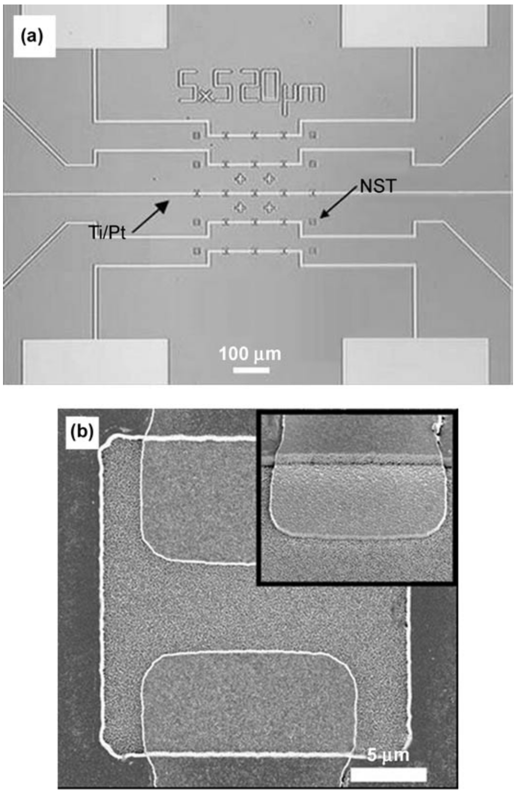

Figure 4. NST-based sensing device showing a) device layout (plan view) and b) metallized NST pad (inset (tilted by 30°): good coverage of metallization on NST).

Figure 6a and b show current variation with time in the presence of H_2. Response S of anatase, an n-type semiconductor, in the presence of H_2 is calculated from Equation (1), where G_0 and G_{gas} are conductance of NST in the

$$S = \frac{G_{gas} - G_0}{G_0} \qquad (1)$$

absence and presence of H_2, respectively. Response of NST to 1 ppm of H_2 at 25 °C was found to be 0.06 with a response time of 417 s (Figure 6a). Response time is defined as that required

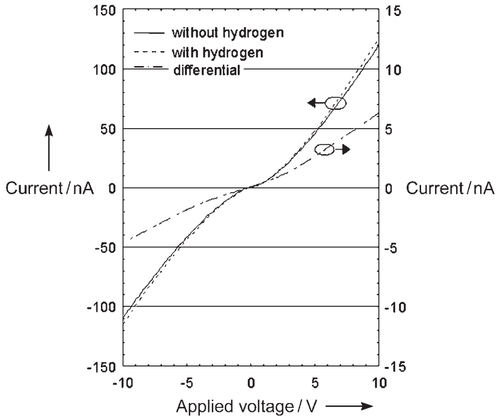

Figure 5. Current–voltage characteristics in vacuum at 25 °C for detection of 1 ppm H_2 gas.

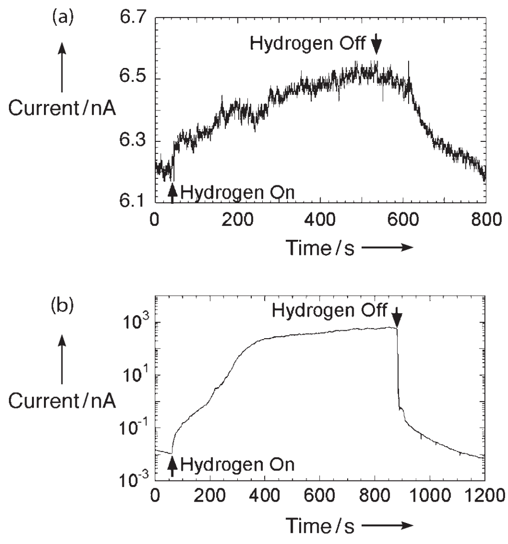

Figure 6. Variation of current with time in the presence of a) 1 ppm H_2 gas in vacuum (25 °C) and b) 4000 ppm of H_2 in synthetic air (275 °C).

for the sensor to reach 90 % of the maximum resistance. The NST-based sensor remains sensitive to H_2 at atmospheric pressure at 275 °C. Current increased by 4.7 orders of magnitude when 4000 ppm H_2 in synthetic air was introduced into the chamber (Figure 6b). However, the response time was increased to 814 s.

Detection of H_2 using undoped titania nanostructures has been reported previously by Grimes et al.[4,13] In their studies, titania nanotubes were formed by anodization and used as elements in sensors. Gaps between electrodes in their devices were about 1–2 mm. Current changes of up to 8.7 orders of magnitude in the presence of H_2 at room temperature were reported. In our present study, the response of 20-μm square NST pads was less pronounced (4.7 orders of magnitude, Figure 6b). When oxygen is present, surface acceptor states are generated and thus a depletion zone is set up. This decreases the NST conductance and results in high base resistance. However, our room-temperature measurements were done in vacuum, where surfaces of NST have less chemisorbed O^- species. This results in a larger density of donor states and lower base resistance. Consequently, when H_2 was introduced into the chamber, the current change was not large. Assuming a base current of about 10 pA if oxygen were present, as observed in Figure 6b, response of the sensor to 1 ppm H_2 can be expected to be about 2.5 orders of magnitude change in current. This is significantly larger than that observed in Figure 6a. Furthermore, to the best of our knowledge, the present study has experimentally demonstrated the lowest detectability limit for H_2 using undoped nanostructured titania. Prior studies detected H_2 at higher concentrations and estimated detectability limit on the basis of linear interpolation of the sensitivity to the concentration corresponding to the measurement resolution of the conductance (or resistance).

Sensitivity of the nanosponge structure is further demonstrated by the increase in current by 4.7 orders of magnitude when NST was exposed to 4000 ppm of H_2 in synthetic air. Sensitivity of NST for H_2 gas is intermediate between those for nanotubes and agglomerates of nanoparticles. As reported by Paulose et al.[13] titania nanotubes have a sensitivity of about 50×10^9 % when exposed to H_2. In comparison, agglomerates of TiO_2 nanoparticles exhibit a sensitivity of about 80 %.[14] As in nanotubular TiO_2,[4,13] we believe the enhanced sensitivity and stability of the nanosponge structure are due to increased electron transport through percolating nanoscopic "necks". This is different from the case of nanoparticle agglomerates, where electron transport occurs at contact points across nanoparticles. In a nanosponge structure, however, there are no contact points. Consequently, there is much less hindrance to electron transport, and this results in higher sensor stability.

The above results show that patterned 3D titania nanosponges can be used as highly sensitive chemical sensors. Moreover, by doping or functionalizing each pad appropriately, sensing properties of individual pads in an array can be tailored, and this will facilitate the realization of multiplex sensing systems such as electronic noses and tongues. Sensing properties can also be tailored by controlling NST morphology by using appropriate Ti film thickness. Electrical isolation, conferred on each NST pad by the amorphous titania phase, is beneficial as it reduces cross-talk, which is crucial for functioning of multiplex sensing systems.

In summary, we have shown that three-dimensionally (3D) interconnected nanosponge titania (NST) is highly sensitive to H_2 gas. Also, we have integrated arrays of titania nanosponges into devices using conventional microfabrication tools. Results of this study suggest that 3D interconnected metal oxide nanostructures are a promising class of sensor materials through which the ultrahigh chemical sensitivity of nanostructures can be harnessed in practical devices.

Experimental Section

The process schematic for integrating NST into devices is shown in Figure 3. An SiO_2 layer (T-SiO_2) was first grown by thermal oxidation of Si. Ti was then deposited, followed by application of another SiO_2 layer (P-SiO_2) by plasma-enhanced chemical vapor deposition. The P-SiO_2 layer was then patterned by lithography. The exposed P-SiO_2

layer after photoresist development was selectively etched in plasma using chlorine chemistry until the underlying Ti layer was exposed. Subsequently, the photoresist layer was dissolved in acetone. The exposed Ti layer was then oxidized in aqueous hydrogen peroxide at 80 °C to form NST. After annealing at 300 °C for 8 h, Ti/Pt metallization was deposited.

Sensing measurements were done in a steel chamber fitted with microprobes for electrical characterization. Applied voltage and current across the NST element were monitored as H_2 was introduced by using mass flow controllers. Assuming hydrogen was entrained in an ideal gas, an equivalent of 1 ppm H_2 was introduced. For H_2 detection at atmospheric pressure, a constant flow of synthetic air (N_2/O_2 mixture) mixed with 4000 ppm of H_2 was introduced at 275 °C.

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