

Highly sensitive gas sensor based on integrated titania nanosponge arrays

A. S. Zuruzi^{a)}

Materials Department, and Mechanical and Environmental Engineering Department, University of California, Santa Barbara, California 93106

A. Kolmakov^{b)}

Chemistry and Biochemistry Department, University of California, Santa Barbara, California 93106

N. C. MacDonald

Materials Department, and Mechanical and Environmental Engineering Department, University of California, Santa Barbara, California 93106

M. Moskovits

Chemistry and Biochemistry Department, University of California, Santa Barbara, California 93106

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Highly sensitive gas sensors were fabricated using nanostructured titania pad arrays. Nanostructured titania (NST) formed is sponge-like consisting of interconnected nanoscale wires and walls, which are made up of anatase nanocrystals. Electrical characterization indicates that contacts were ohmic and NST was highly sensitive to O₂. Variations of hundreds of oxygen molecules over a 20 μm NST square pad sensing element were detected at 250 °C. The NST-based sensor operates at lower temperatures, has fast response time, and superior sensitivity relative to oxygen sensors based on porous undoped titania reported in the literature. © 2006 American Institute of Physics.

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Due to their large surface to volume ratios nanostructured materials have been predicted and demonstrated to be excellent candidates for ultrasensitive and highly miniaturized sensors.¹ Recent studies have focused on discrete nanostructures such as single-walled carbon nanotubes,² silicon nanowires,³ palladium mesowire arrays,⁴ metal oxide nanowires/nanobelts,^{5–7} and polymeric nanowires.^{8,9} Also, the invention¹⁰ and application¹¹ of novel technologies such as “dip pen” lithography, development of complex nanostructured materials,¹² and new methods for their deposition^{13–15} have had a profound impact on traditional “top-down” methodology.

In this vein we propose a new approach in which micrometer-scale patterned sponge-like structures consisting of interconnected nanoscale walls or wires are used as elements for gas sensing. Configured as active elements of a conductometric¹⁶ sensing device, these structures possess the ultrahigh sensitivity of nanostructures and are amenable to integration into real world devices. Here, we demonstrate this approach by fabricating a gas sensor utilizing arrays of nanostructured TiO₂ (NST) pads as sensing elements. TiO₂ is chosen as it has been widely studied for sensing applications and its chemical specificity toward many gases can be tailored by judicious use of surface activation and dopants.^{17–21} TiO₂ can also be made porous and the pore structure controlled which allows functionalization with biomolecules and promises applications in biological sensing.²²

Sensing devices were fabricated as follows. A 500 nm thick Ti film was first evaporated on an SiO₂ (T-SiO₂) layer thermally grown on Si. Another SiO₂ (P-SiO₂) layer was then deposited on the Ti layer using plasma-enhanced chemi-

cal vapor deposition. The P-SiO₂ layer was subsequently etched exposing Ti patterns which were then oxidized in aqueous 10% hydrogen peroxide at 80 °C. After annealing at 300 °C, Ti(10 nm)/Pt(250 nm) electrodes were evaporated. Morphology and phase evolution of TiO₂ formed was studied using a variety of techniques.²³ Gas sensing experiments were carried out in a vacuum chamber (3000 cm³ total volume) equipped with microprobe contacts for current-voltage (*I-V*) measurements. Oxygen pressure in the chamber was controlled using a pulsed needle valve and verified using an ion gauge. The sensor assembly was heated to the desired temperature using a halogen lamp and confirmed using a thermocouple.

NST formed has porous structure consisting of interconnected nanoscale walls and wires (Fig. 1). For unpatterned NST layers formed from unpatterned Ti surfaces, a mud-crack pattern was observed [Fig. 1(b)]. Similar mud crack patterns had been observed during oxide film formation and thermal cycling.²⁴ When samples are dried in air and moisture evaporates, cracks form due to development of biaxial

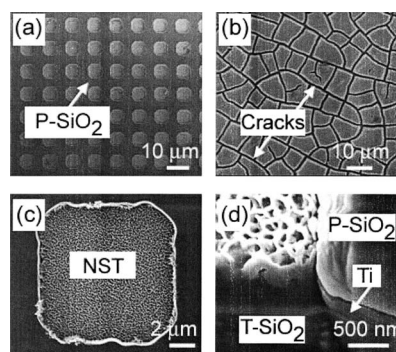


FIG. 1. (a) Arrays of crack-free 5 μm square pad; (b) crack-filled blanket NST; (c) a 10 μm square NST pad; and (d) edge of a pad after focus ion beam milling revealing the porous structure.

^{a)}Present address: Intel Corp., 5000 W. Chandler Blvd., Chandler, AZ 85226; electronic mail: zuruzi.abu.samah@intel.com

^{b)}Present address: Physics Department, Southern Illinois University, Carbondale, IL 62901.

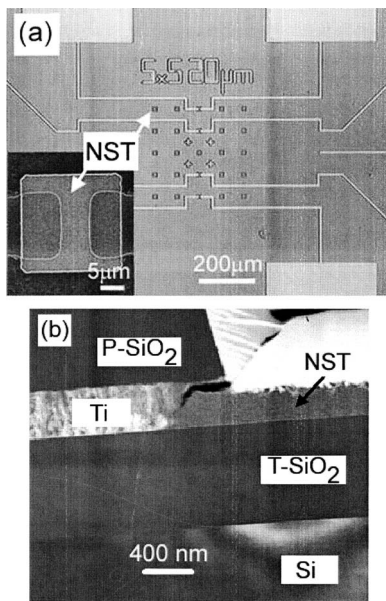


FIG. 2. (a) Optical micrograph of sensor utilizing patterned integrated NST arrays as sensing elements (Inset) scanning electron microscope image of a single metallized NST pad and (b) cross-sectional TEM of an NST pad showing fully oxidized NST layer.

tensile stress. For a given film thickness of the NST layer, crack formation ceases if the size of the Ti pads is smaller than a characteristic dimension; in our case this dimension is $50\ \mu\text{m}$. For arrays of 5 and $20\ \mu\text{m}$ square pads, only 0.8% and 4%, respectively (of 500 pads) developed cracks [Figs. 1(a) and 1(b)]. For $50\ \mu\text{m}$ square pad arrays, all NST pads developed cracks.²³ Pores extend to the $\text{TiO}_2/\text{T-SiO}_2$ interface indicating complete oxidation of exposed Ti surfaces [Fig. 1(d)].

In the present study, only $20\ \mu\text{m}$ crack-free NST pads were used as elements in gas sensors. Figure 2(a) shows a gas sensor consisting of a 5 by 5 array of $20\ \mu\text{m}$ NST pads. Although the NST pads are porous, satisfactory electrical contacts were obtained, evidenced by their ohmic nature as discussed below. Cross-sectional transmission electron microscopy (TEM) shows metallization penetrating only a few nanometers into the pad [Fig. 2(b)]. Selected area electron diffraction (SAED) of the exposed NST regions consists of sharp concentric rings assignable uniquely to polycrystalline anatase. Presence of anatase was confirmed by x-ray diffraction.²³

Figures 3(a) and 3(b) show electrical characteristics of an NST pad in vacuum and under exposure at various O_2 pressures ranging from 0.3 to 0.8 mTorr, respectively. The linear I - V characteristics indicate the ohmic nature of contacts between Ti/Pt electrodes and NST pads. Conductance of NST pads is sensitive to the presence of oxygen and changes monotonically with oxygen pressure. At 0.3 mTorr O_2 pressure, conductance is approximately 1 order of magnitude less than that in vacuum (no oxygen gas). This high sensitivity to O_2 is also illustrated in Fig. 3(b) where O_2 pressure variations in the sub-mTorr range are easily distinguishable. Assuming O_2 to be an ideal gas and using the equation of state for ideal gases, variations in sub-mTorr O_2 pressure indicates the ability to detect variations of about a few hundred O_2 molecules over a $20\ \mu\text{m}$ NST square pad. Although the focus of the present study is detection of oxy-

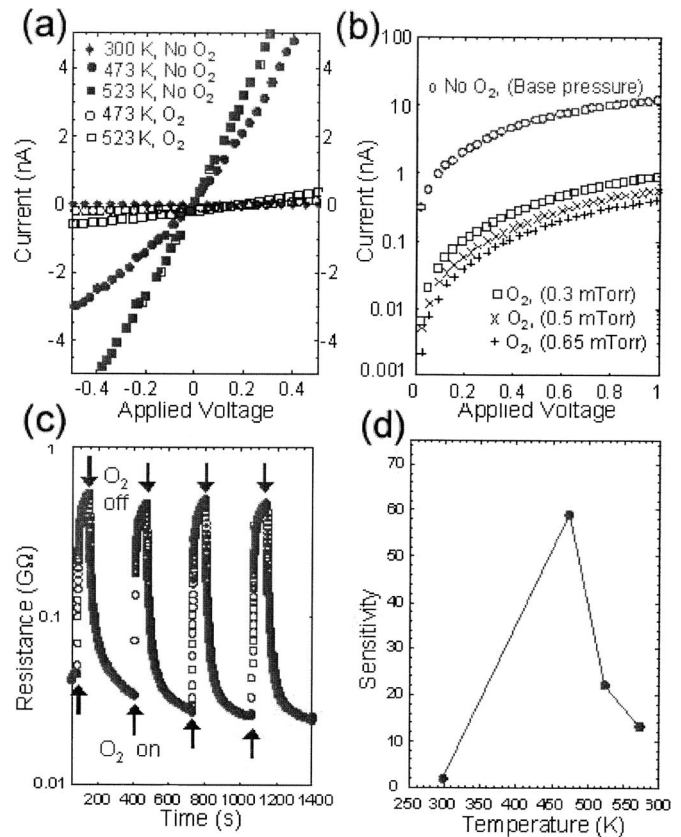


FIG. 3. Current-voltage characteristics in: (a) N_2 and O_2 at 0.8 mTorr; (b) O_2 at various pressures; (c) Resistance change with oxygen cycling; and (d) sensitivity at various temperatures.

gen at sub-mTorr O_2 pressure, the sensor was also able to detect oxygen at a few mTorr.

Resistance of an NST pad changes when exposed to oxygen cycles at 473 K [Fig. 3(c)]. At 0.8 mTorr, resistance increased from 10% to 90% of the maximum value in 48 s. This time duration, usually referred to as response time, is comparable to those of other oxygen sensing devices utilizing porous undoped titania as a sensing material. Sharma *et al.* have fabricated porous undoped titania films using various techniques. The resulting titania films have pore size distribution ranging from ~ 0.5 to 1.5 and 0.75 to $2.5\ \mu\text{m}$.^{25,26} The response times reported were obtained at higher temperatures. To compare these response times with the values obtained in the present study we assumed that response times depend on temperature in an Arrhenius fashion.²⁷ For the titania films with ~ 0.5 – 1.5 and 0.75 – $2.5\ \mu\text{m}$ pores, the response times at 523 K were calculated to be 43 and 16 s, respectively. The former value is close to that obtained in this study. Sensitivity of a sensor is defined as the ratio of the maximum resistance in the presence of oxygen to the resistance in the absence of oxygen.^{25,26} Optimal sensitivity of NST-based sensor (60 at 523 K) is superior to those of undoped-titania based sensors reported. Sharma *et al.* and Gao *et al.* reported sensitivity values of 1.43 and ~ 30 at higher operating temperatures^{25,26,28}—these values would reduce accordingly at 523 K. In addition, an important advantage of the present approach is minimal drift with time of electrical properties of NST-based sensors. This could be due to the high crystallinity of NST formed as indicated by SAED studies.²³ The ability to detect low oxygen partial pressures makes the sensor

suitable for applications such as *in situ* detection of oxygen content during high-vacuum deposition of complex oxides.

Undoped TiO₂ shows *n*-type semiconducting behavior due to the presence of shallow intrinsic donors. Below 1273 K, the dominant donor species are singly and doubly ionized oxygen vacancies, with associated defect levels located just below the conduction band.^{29,30} For TiO₂-based sensors, the resistance change upon O₂ exposure is due to the interplay between the ionic chemisorption of oxygen at the TiO₂ surface and the density of carriers in the material's conduction band. Upon adsorption, an O₂ molecule migrates to an oxygen vacancy site,³¹ where it interacts with surface vacancies eventually forming chemisorbed species such as O₂⁻, and O⁻ (depending on temperature). The process involves electron transfer across the titania surface and depleting the electron density of the bulk TiO₂. The net decrease in conduction is due to annihilation of the donor states. At elevated temperatures the oxygen-induced vacancy annihilation process could involve subsurface and even bulk donors.^{25,26} Hence, for enhanced sensing performance, materials with structures that allow the permeation of oxygen through a porous sensing element with a large surface area and thin channels are desirable. NST is porous with wall thickness of 25–75 nm. This porous structure has a large surface area for sensing. However, compared to porous TiO₂ in a previous report²⁵ the pore size of NST used in the present study—which ranges from 50 to 200 nm—is ~10 times smaller. Since oxygen gas permeation is reduced for smaller pore sizes, one would expect NST to have lower oxygen gas permeation and, consequently, a longer response time. However, the response times at 523 K are similar. In addition, the NST-based O₂ sensor exhibits superior sensitivity compared to those in Ref. 25. These observations suggest that the enhanced oxygen sensing performance of NST is due to a higher level of surface reactivity, possibly due to the presence of a greater number of surface defects.

In conclusion, we have described a method for forming arrays of crack-free nanostructured titania (NST) pads which could be used as sensing elements. This method uses existing process tools and materials and hence is compatible with current microelectronics manufacturing practices. Using patterned Ti thin films with lateral dimensions below a certain threshold, crack formation in NST layers can be eliminated. A prototype sensor using a 20 μm NST square pad as a sensing element was able to detect variations of hundreds of oxygen molecules at 250 °C. The NST-based sensor operates

at lower temperatures, has a fast response time, and superior sensitivity relative to oxygen sensors based on porous undoped titania in the literature.

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