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Fabrication, Structural Characterization and Testing of a Nanostructured Tin Oxide Gas Sensor

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Abstract—A nanostructured SnO₂ conductometric gas sensor was produced from thermally evaporated Sn clusters using a thermal oxidation process. SnO₂ clusters were simultaneously formed in an identical process on a Si₃N₄ membrane featuring an aperture created by a Focused Ion Beam (FIB). Clusters attached to the vertical edges of the aperture were imaged using a transmission electron microscope. The original morphology of the Sn cluster film was largely preserved after the thermal oxidation process and the thermally oxidized clusters were found to be polycrystalline and rutile in structure. Further, secondary ion mass spectrometry and X-ray photoelectron spectroscopy were used to establish the levels of nitrogen present in the films following exposure to NO₂ gas.

Index Terms—Gas detectors, microscopy, nanotechnology, thin-film devices.

I. INTRODUCTION

RUBILE tin oxide (SnO₂) is a wide band-gap n-type semiconductor which has been employed as a gas sensing material for many years [1]. Adsorption of oxidants or reducing agents on the SnO₂ surface causes a change in the depth of the electron-depletion layer below the surface and a corresponding change in the resistance of the material. For example, if a film of SnO₂ at a temperature between 100 °C and 500 °C is exposed to NO₂ gas, ionosorption of oxygen (in its molecular and atomic forms) occurs and the depletion layer width increases [2], [3]. This produces a concentration dependent increase in resistance and thereby provides the sensing mechanism. A change in the operating temperature of a SnO₂ sensor produces changes in the rates of the surface adsorption and desorption processes and a change in the energy required to activate them. Consequently, the sensitivity of SnO₂ to oxidizing and reducing gases is temperature dependent [3]. Nanostructured SnO₂ sensors have been produced by various research groups, as their surface-to-volume ratio is large and the gas-surface interaction can take place on both sides of a grain or neck instead of only on the top surface, as in the case of a compact film [2]. With careful process control, feature sizes can be made comparable to the depth of the depletion layer. This can yield very high sensitivity since pathways through the conducting network can become completely “pinched-off” above a certain exposure level. The effects of the feature (grain) size have been studied in detail by various authors (see, for example, [2]–[4]). Despite the growing number of techniques for producing nanostructured SnO₂ sensors, it is widely acknowledged that the relationship between the electrical and nanostructural properties of SnO₂ gas sensing films is not yet fully understood [2].

Physical vapor deposition methods used to produce SnO₂ films include pulsed laser deposition [5], sputtering [6], and evaporation [7]. It is also possible to deposit Sn films in an inert atmosphere, and subsequently transform them into SnO₂ using a thermal annealing process. The rheotaxial growth and thermal oxidation (RGTO) process [7], [8] is commonly used to transform porous Sn thin-films into SnO₂ as the morphology of the original film is substantially retained after the transformation. The technique has also been employed to produce SnO₂ nanowires from Sn nanowires [9]. In this method, the Sn sample is heated in the presence of oxygen to a temperature just below the Sn melting point to promote growth of a native oxide shell. The oxide shell retains its shape during a high-temperature oxidation process (typically, 600 °C–700 °C) which follows and thus the morphology/dimensions of the film/nanowire can be preserved. Using cross-sectional transmission electron microscopy (TEM), we recently confirmed that the morphology of the Sn cluster film remained largely unaltered after the RGTO process [10] and that full conversion to SnO₂ was achieved using a 600 °C oxidation temperature.

In this work, we have fabricated a nanostructured RGTO processed SnO₂ sensor and determined its sensitivity to NO₂ gas over an operating temperature range of 25 °C to 290 °C. A novel sample preparation method enabled TEM imaging of the SnO₂ film before and after oxidation. High-resolution images of the interior of SnO₂ clusters were obtained without sectioning samples using this technique. Secondary ion mass spectrometry and X-ray photoelectron spectroscopy were then used to measure the nitrogen content in the films.
II. EXPERIMENT

A. Sample Preparation

The SnO$_2$ films were deposited on P-type Si substrates with a 1-$\mu$m-thick layer of SiO$_2$ separating the SnO$_2$ layer from the Si substrate. Planar electrical contacts on the sensor were fabricated using a photo-plot mask and optical lithography. The total length of each interdigital-type contact was approximately 35 mm and the contact-to-contact separation was approximately 100 $\mu$m.

The Si$_3$N$_4$ membranes (designed to fit into a standard TEM sample holder) were purchased from SPI Supplies [11]. Slots with $\sim$330 $\mu$m width and 25 $\mu$m length were etched through the 50 nm thick membranes (as shown in Fig. 1) using a FEI Nova Focused Ion Beam system with an ion beam dose of 0.1 nC/$\mu$m$^2$ at 0.2 pA beam current.

B. Deposition of Sn and Thermal Oxidation to Form SnO$_2$

The membrane and contacted substrate were mounted in the deposition chamber of a Dynavac thermal evaporator. In order to ensure that the samples experienced identical deposition conditions, they were situated in close proximity to each other. The deposition rate was $0.2 \pm 0.05$ nm/s (measured using a quartz crystal film thickness monitor) and the base pressure and process pressure were $1 \times 10^{-6}$ Torr and $5 \times 10^{-6}$ Torr, respectively. After depositing a Sn layer of nominal thickness 80 nm, the coated sensor substrate and Si$_3$N$_4$ membrane were heated in air at atmospheric pressure using a simple bench-top furnace. The temperature sequence for the thermal oxidation was temperatures up to 300 $^\circ$C (2 h), then 400 $^\circ$C (2 h) and, finally, 600 $^\circ$C (2 h) with 30-min ramp times between each temperature. Once complete, the SnO$_2$ coated sensor substrate was placed in a multichannel gas calibration system. The contact-to-contact resistance was then measured in synthetic air and during timed exposures to various concentrations of NO$_2$ gas (provided from a bottle consisting of 8.5 ppm NO$_2$ in dry synthetic air).

C. Microscopy and X-Ray Photoelectron Spectroscopy

A JEOL 2010 TEM operating at 200 kV was used to provide images of the nanostructure within the clusters. Fig. 2 shows schematically how the Sn coated Si$_3$N$_4$ membrane samples were positioned in the TEM and how images of clusters on the vertical walls of the etched slot were obtained. X-ray photoelectron spectroscopy (XPS) was also performed on the Sn and SnO$_2$ cluster films using a VG MicroLab 310 F with a 1486.6 eV Al anode X-ray source operated at a power of 300 W and with a 15 kV excitation voltage. The samples were tilted such that the electron analyzer was normal to the sample surface. The analyzed rectangular area was approximately $5 \times 1 \ \text{mm}^2$. All samples were sputtered in situ with Ar ions in order to remove carbon contaminants from the surface. A SnO$_2$ powder standard [12] was used to calibrate the sensitivity factors prior to the measurements. The scan was centered over the Cls, Sn3d, and O1s binding energy peaks with a pass energy of 20 eV and an energy step size of 0.1 eV. A Sn3d5 sensitivity factor of 21.00 was determined to be correct.

Depth profiling of the nitrogen levels within the samples was performed by sputtering away the sample in situ using a 3 kV Ar sputtering beam. A broad spectrum scan was acquired using a pass energy of 50 eV and energy step size of 0.1 eV. The areas under the N1s and Cls peaks were fitted, and sensitivity factors from the Scofield (Al Source) library [13] were applied to determine the relative atomic percentages of nitrogen and carbon through the depth of the samples.

D. Secondary Ion Mass Spectroscopy (SIMS)

A Cameca 5 f Dynamic Secondary Ion Mass Spectrometer (SIMS) was used to determine the composition of the SnO$_2$ films. Specifically, a depth profile of the nitrogen content was measured for three films prepared under identical conditions but having different exposures to NO$_2$ gas. Cs$^+$ ions were used to probe the sample at normal incidence and the primary accelerating voltage was 2.4 kV. The beam diameter was 20 $\mu$m and the analyzed area was approximately $250 \times 250 \ \text{mm}^2$. The total acquisition time per sample was approximately 800 s.

E. Gas Sensing Measurements

The sensor was mounted on an alumina microheater in the test multichannel gas chamber. The microheater was controlled by a regulated DC power supply and provided operating temperatures up to 300 $^\circ$C. A gas calibration system, with computer interfaced mass flow controllers, was used to expose the sensor to different concentrations of NO$_2$ gas. The sensor resistance was measured continuously using a multimeter (Keithley 2001) that was also interfaced with a personal computer. The total flow rate was kept constant at 200 sccm and since SnO$_2$ is sensitive to humidity [14], synthetic air (certified zero humidity) was used as the reference gas.
III. RESULTS AND DISCUSSION

A. TEM Characterization of SnO$_2$ on Si$_3$N$_4$ Membranes

Fig. 3 shows a Sn cluster film supported on a Si$_3$N$_4$ membrane and imaged immediately after the deposition process. Significant coalescence between neighboring clusters caused the Sn films on the sensor and Si$_3$N$_4$ membrane to appear coral-like in morphology, however, discrete clusters could still be found under the TEM. The average cross-sectional area of these clusters was measured using image processing software and found to be approximately 1 x 10$^4$ mm$^2$. As shown in Fig. 3(b), the as-deposited Sn films contained irregular shaped clusters with thin surface oxide shells surrounding the Sn cores. The majority of the oxide layer would have grown after the Si$_3$N$_4$ membrane was removed from the vacuum deposition system.

Following oxidation at 600 °C, the discrete cores and oxide shells were no longer visible and the nanostructure of the SnO$_x$ clusters became more complex, containing small voids and crystallites (Fig. 4). The crystallites observed in the oxidised clusters had cross-sectional areas of between 5 mm$^2$ and 500 mm$^2$. Selected area diffraction patterns from the as-deposited and oxidized Si$_3$N$_4$ membrane samples (not shown) could be indexed to metallic Sn and rutile SnO$_2$, respectively. The TEM images and diffraction patterns showed no preferred orientation of the SnO$_2$ and no evidence could be found for metallic Sn reflections in the diffraction pattern from the oxidized sample, indicating that the Sn clusters had fully transformed into SnO$_2$ after the oxidation process. This assertion was supported using XPS which showed that Sn, SnO and SnO$_2$ were present in the as-deposited sample but only SnO$_2$ was present after oxidation [10].

Fig. 5 shows the same area of the membrane/film before [Fig. 5(a)] and after [Fig. 5(b)] thermal oxidation. In Fig. 5(a), the clusters consist of Sn cores with oxide shells (as in Fig. 3), while in Fig. 5(b), the clusters consist of polycrystalline SnO$_2$ but largely retain their original shape. Unlike conventional TEM samples, the Si$_3$N$_4$ membrane can be fabricated quickly and the sensing film can be imaged immediately after each process without exposure to epoxy or other chemicals. Importantly, the Si$_3$N$_4$ membrane withstood the FIB etching, the thermal oxidation process and numerous transfers between microscopes and deposition systems. Inspection of thermally treated nanoparticles/nanowires composed from other materials should therefore be possible using this method.
B. Gas Sensing Measurements

The normalized change in the resistance of the SnO$_2$ gas sensor during exposure to various concentrations of NO$_2$ and at three different operating temperatures is shown in Fig. 6. The sequence of NO$_2$ concentrations inlet to the sample chamber was 510 ppb, 1.06 ppm, 2.12 ppm, and a repeat 1.06 ppm. Each concentration was inlet as a pulse in between periods in which synthetic air was inlet to the chamber. The difference in the baseline resistance (with no NO$_2$ gas present) before and after each sequence of NO$_2$ pulses was less than 5% in the temperature range 150 °C–290 °C and the reproducibility in response was within 15% in the same temperature range. A film exposed for 36 h to 2120 ppb of NO$_2$ at 265 °C did, however, exhibit a significant permanent increase in its baseline resistance (in synthetic air) from 4.6 kΩ (before exposure) to 5.2 kΩ (after exposure).

The maximum measured sensitivity was observed at a temperature of 210 °C (see Fig. 7), while the minimum response and recovery times occurred when the sensor was operated at 265 °C. With an NO$_2$ concentration of 510 ppb, these times were 45 s and 30 s, respectively, at 265 °C, and 180 s and 130 s, respectively, at 210 °C.

These results are consistent with previously observed sensing behavior in porous SnO$_2$ films which exhibit an asymmetric bell-shaped variation of the gas sensitivity with the sensor operating temperature [15]. The temperature at which the maximum sensitivity occurs is also dependant on the concentration of the gas [15]. The resistance changes observed in the sensor are due to the temperature dependant chemisorption of NO$_2$ at the surface of the SnO$_2$. If electronegative NO$_2$ molecules approach the surface of the SnO$_2$ with electron affinities greater than the semiconductor work function, the molecules will each pick up an electron from the SnO$_2$ conduction band and become chemisorbed at the surface. The width of the electron depletion layer and the height of potential barrier that surround the SnO$_2$ clusters both increase as a result of the increased surface charge [16].

The thickness of the depletion region within the clusters is reduced at high-temperatures due to an increase in thermal ionization, and hence carrier concentration [17]. As a result, the proportional change in the thickness of the nondepleted region (within each cluster/neck) may be lower at higher temperatures, contributing to a smaller change in the normalized resistance. The response and recovery times decrease with increasing temperature because the thermally activated adsorption and desorption processes occur (and balance out to equilibrium) more rapidly [17] and because the penetration of the gas into the sensing layer decreases [15].

C. SIMS and XPS Measurements

SIMS was used to measure the relative amounts of nitrogen in a “high-exposure” sample (≈ 36-h with 2120 ppb NO$_2$ at 265 °C), a “low-exposure” sample (12 h with 2120 ppb NO$_2$ at 265 °C), and a nonexposed, nonheated SnO$_2$ cluster film. The results are shown in Fig. 8. In the SIMS process, approximately 100 s of etching was required to remove surface contaminants (expected to be predominantly carbon) from the porous tin oxide layer. The measurements taken after this period clearly show that increased exposure time led to increased retention of nitrogen in the SnO$_2$ cluster films. This may have contributed to the ~ 5% change in the baseline resistance observed in the “high-exposure” sample. In order to quantify the nitrogen trace derived from SIMS, XPS depth profiling was performed. Fig. 9(a) shows a XPS depth profile from the nonexposed, non-heated SnO$_2$ film and Fig. 9(b) shows a XPS profile from the “low-exposure” (12 h with 2120 ppb NO$_2$ at 265 °C) SnO$_2$ film.
film. As in the SIMS measurements, a significant contamination level existed at the surface so the nitrogen levels were measured after this contamination layer was removed. The average level of nitrogen in the subsurface of the low-exposure sample was found to be 1.8%, compared to 0.85% for the unexposed sample. Using this data as a basic calibration suggests that the nitrogen level in the sensor was greater than 3%.

IV. CONCLUSION

The RGTO technique was used to prepare SnO$_2$ clusters from discontinuous evaporated Sn thin films on a conductometric sensor substrate and a Si$_3$N$_4$ membrane featuring an aperture-slot. The temperature dependent response of the SnO$_2$ conductometric gas sensor was measured for various concentrations of NO$_2$ gas. Transmission electron microscopy of Sn and SnO$_2$ clusters adhered to the walls of the aperture-slot was performed before and after the thermal oxidation process. Selected area diffraction analysis showed that after oxidation at 600 °C, the clusters were transformed to polycrystalline rutile SnO$_2$. The estimated volumetric change of the clusters after oxidation was ~ 50% but the morphology of the cluster films was largely preserved after the RGTO process. The slotted membrane method provided similar information to cross-sectional TEM but with greatly reduced sample preparation time. This method could also be employed to inspect clusters made from a wide variety of materials and deposited using a variety of physical vapor deposition or wet-chemical techniques. The significant retention of nitrogen found using SIMS and XPS may be a contributing factor in the “ageing” effects (changing baseline resistance) commonly observed in nanoporous SnO$_2$ sensors and warrants further investigation.

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