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Electronically addressable SnO_2 inverted opal gas sensors fabricated on interdigitated gold microelectrodes

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Electronically addressable thin films of tin oxide gas sensors with well-defined opaline microstructures and reproducible sensor-to-sensor responses have been fabricated on interdigitated gold microelectrodes through self-assembly growth of a monodisperse polystyrene latex film onto the electrodes followed by infiltration of tin *tert*-butoxide and calcination of the film.

Colloidal crystals of silica and polystyrene have gathered interest in the past several years as templates for inverted opaline materials ranging from metals to ceramics and polymers.[1] A great deal of this research has been directed towards an examination of the photonic properties of these materials, especially towards the synthesis of high-refractive index materials which would possess a complete band gap in the visible and near-infrared regime.[2,3] Electroactive opaline materials also have been studied for applications ranging from ferroelectric photonic switches[4] to novel battery electrode architectures which offer both electrochromic tuning of the Bragg stop bands and greater mass transport.[5,6]

We have shown previously that inverted opals and opals of SnO_2, a common solid state gas sensor, are useful as well-defined microstructures, thereby allowing structure–property relationships to be examined.[7] The sensor properties of inverted SnO_2 opals, in particular, appeared near to the theoretical ideal. However, previous fabrication of sensors involved the deposition of opaline SnO_2 powders onto interdigitated gold electrodes, leading to deviations from ideal behaviour due to random porosity. It was desirable to be able to grow these structures directly within the interdigitated arrays, thereby promoting sensor-to-sensor reproducibility as well as ideal sensor responses. Previous work within our group showed that planarized colloidal crystals can be grown within microchannels utilizing directed evaporation induced self-assembly (DEISA).[8] This novel directed colloidal-assembly technique allows high-quality polystyrene opaline films of controllable thickness, geometry and orientation to be grown within interdigitated arrays, which can then be used as templates to form inverted opaline films electronically addressed by the gold microelectrodes. To our knowledge the only other example of colloidal crystal films grown between electrodes involves the fabrication of colloidal films between ITO plates utilizing large silica colloids as spacers.[9]

Films of polystyrene colloids were grown on interdigitated electrode arrays consisting of forty 15 μm gold electrodes with 15 μm spacing and a height of 100 nm on a borosilicate glass substrate (ABTECH Scientific, Inc.) as well as gold electrode arrays with 40 μm spacing on alumina substrates with a Pt heater element on the reverse side of the alumina tile (Capteur Sensor). The number of colloid layers could be controlled through the concentration of polystyrene spheres. A typical preparation consisted of 10 mg of a 10% by weight surfactant-free polystyrene colloid solution (sphere size *ca.* 360 nm) added to 10 g of absolute ethanol.[10] The electrode array was placed in the solution perpendicular to the air–water interface, and DEISA driven growth of the polystyrene colloidal film proceeded through capillary forces due to the evaporation of ethanol under ambient conditions. Fig. 1 shows FE-SEM micrographs of two colloidal films grown on interdigitated gold arrays consisting of monolayer and three-layer growth. The gold electrode can be seen at the top and bottom of the micrograph of the monolayer polystyrene film. Without exception the films grew as well-ordered, fcc-lattices with the (111) plane parallel to the substrate surface. The 100 nm step height at the electrode boundary was found to induce line defects in the polystyrene films, as can be seen in the three-layer film in Fig. 1. Cracks seen in the films formed during exposure to the electron beam.

The polystyrene opal films were then placed in a 90 °C oven for one hour to introduce moderate necking between spheres. This was found to improve the adhesion and structural stability of the subsequent tin oxide inverse opal films. Tin *tert*-butoxide was infiltrated into the films under vacuum followed by hydrolysis-condensation of the alkoxide in air for one day. Films were then calcined under air at 500 °C to remove the polystyrene template. Fig. 2 shows the FE-SEM micrographs of inverted SnO_2 opaline films fabricated from polystyrene colloidal films of monolayer coverage and three-layer coverage, respectively. The films are quite well ordered, although some fractures are seen in the films after calcination. These fractures are introduced during the 25% shrinkage of the inverted opal structure as the amorphous tin oxide structure crystallizes.[1d,7a] PXRD of the resulting films shows they consist of nanocrystalline cassiterite with an estimated average crystallite size of approximately 7 nm using the Scherrer equation. The periodicity and crystallite sizes of the final inverted SnO_2 opals calcined at 500 °C agree with values obtained for bulk inverted SnO_2 opals.[7a]

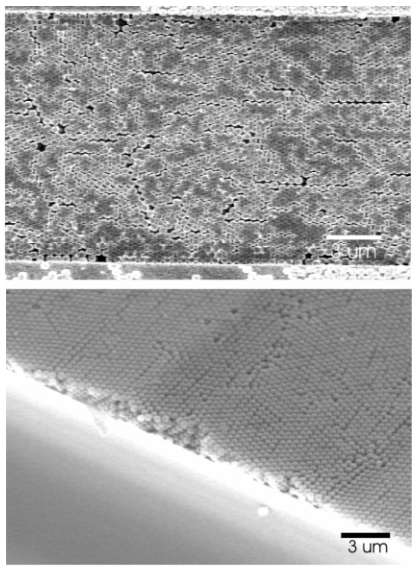

Fig. 1 FE-SEM micrographs of polystyrene films grown by the DEISA method[8] on interdigitated gold electrodes. The top image corresponds to monolayer coverage; the lower is a cross-section of a three-layer film.

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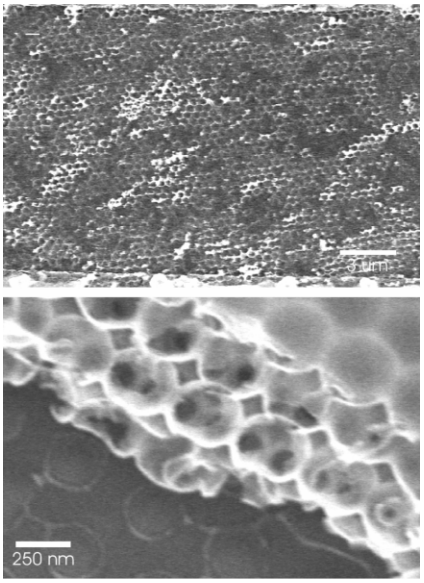

Fig. 2 FE-SEM micrographs of inverted SnO_2 opal films grown on interdigitated gold electrodes. The top image corresponds to a monolayer film; the lower shows the cross-section of a three-layer film.

In order to investigate the sensor response of these inverted SnO_2 opal films, three layer films on the alumina substrate were heated to 400 °C using the Pt heater element and the AC-impedance response was measured in air and 2000 ppm CO. Fig. 3A shows a representative AC-impedance response of the electrode array in air and carbon monoxide. The single arcs seen by AC-impedance indicate that the contacts between the film and the gold electrode are sufficient as no charging interactions are seen. Fig. 3B shows the DC response of a sensor over several air/CO cycles; the sensor response is quite rapid and reproducible. Several arrays were fabricated and all showed nearly identical sensor responses towards carbon monoxide: the sensitivity towards 2000 ppm carbon monoxide was $G = (R_0 - R)/R = 4.3 \pm 0.1$ where R is the resistance in CO and R_0 is the baseline resistance in air. In comparison, bulk SnO_2 inverted opaline powders deposited onto arrays with an organic vehicle (ESL 400; Agmet Ltd.) gave similar sensitivities towards 2000 ppm CO ($G = 5.1 \pm 0.7$) but with much larger deviations between samples due to random porosity generated by the vehicle.[7a] Precise control of microstructure is crucial during the fabrication of solid-state metal oxide gas sensors: small variations in the fabrication of sensors from SnO_2 powders, such as the ratio of oxide to organic vehicle, can lead to large differences in sensor responses.[11] Through this integration of the SnO_2 synthesis and sensor fabrication, sample to sample differences in sensor behaviour are minimized due to the well-controlled opaline microstructures present between adjacent gold electrodes. Some disorder still exists due to the fractures formed during calcination: we believe this has a smaller effect on the sensor to sensor reproducibility as there are still a large number of uninterrupted connections between electrodes.

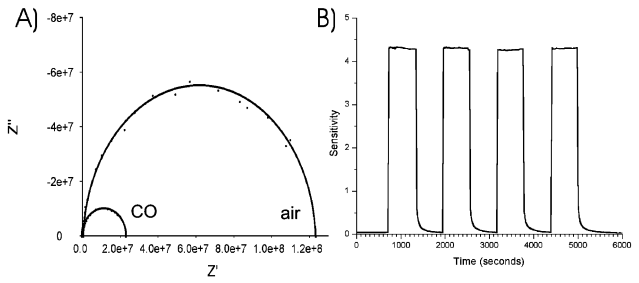

Fig. 3 Response of inverted SnO_2 opal film within the microelectrode array to dry air and 2000 ppm carbon monoxide examined by (A) AC-impedance and (B) DC methods showing reproducibility of response over several air/CO cycles.

Opaline films with a high degree of ordering at the electrode interface can also be formed by the sedimentation of aqueous polystyrene colloid solutions on the interdigitated electrodes, though little control of film thickness is achievable by this method. However, sedimentation of polystyrene colloids onto the interdigitated gold electrodes followed by the inversion of the structure to form inverted metal oxide opals allows for possible large-scale fabrication of sensor arrays, which have well-defined microstructures at the electrode interface. The fabrication of inverted opaline films of metal oxides is a realistic and cost-effective alternative strategy to form sensor arrays with reproducible sensor-to-sensor responses.

We are further investigating the possibility of co-assembling nanocrystalline SnO_2 colloids and polystyrene spheres as a route to avoid the cracks formed in the inverted SnO_2 opaline films due to shrinkage of the amorphous tin oxide structure upon calcination.[12] This should allow for the formation of near-perfect replicas of the original polystyrene colloidal crystal film. Another avenue of improvement is the fabrication of custom-designed interdigitated electrode arrays by soft-lithography techniques in which the dimensions of the array can be varied. Changing the height of the gold electrodes to allow the complete packing of multi-layers of colloids within the grooves should help minimize the number of defects in the films and allow for the growth of different colloidal crystal geometries.[8]

In summary, in this preliminary Communication we report a novel, facile and convenient way of fabricating inverted SnO_2 opaline films within interdigitated electrode arrays, and have examined the sensor response of these films towards carbon monoxide. This assembly technique allows for the fabrication of well-defined opaline microstructures, which have reproducible sensor-to-sensor responses. While we have focussed on the design of opaline SnO_2 films, in reality this method is quite versatile and can be applied towards the fabrication of controlled microstructures of a wide range of metal oxides, metals, and polymers. Indeed, we are investigating the use of such fully-integrated arrays for applications ranging from pre-assembled photonic switches to battery electrodes.[4–6]

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Notes and references

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