

Microsphere templating as means of enhancing the sensitivity of thin film metal-oxide gas sensors

Avner Rothschild*, Il-Doo Kim**, Takeo Hyodo***, and Harry L. Tuller****

*Department of Materials Science and Engineering, MIT, Cambridge, MA, USA, avner@mit.edu

**Optoelectronic Materials Research Center, KIST, Seoul, Republic of Korea, idkim@kist.re.kr

***Dep. Mater. Sci. & Eng., Nagasaki University, Nagasaki, Japan, hyodo@net.nagasaki-u.ac.jp

****Department of Materials Science and Engineering, MIT, Cambridge, MA, USA, tuller@mit.edu

ABSTRACT

Chemical and physical synthesis routes were combined to prepare macroporous thin films of semiconducting metal-oxides such as $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and TiO_2 by pulsed laser deposition onto poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) microsphere templated substrates. Subsequently, the organic microspheres were removed by thermal decomposition. The remaining inorganic films comprised a monolayer of hollow hemispheres with diameter commensurate with that of the microspheres. This unique morphology increases the surface area and reduces the interface area between film and substrate. Consequently, the surface activity is markedly enhanced while deleterious interfacial effects between film and substrate are significantly reduced. Both effects are highly advantageous for gas sensing applications. Indeed, microsphere templated films showed remarkably enhanced gas sensitivity compared with control films deposited onto untreated substrates.

Keywords: colloidal templates, microspheres, gas sensors, thin films, macroporous

1 INTRODUCTION

The pursuit of new materials with novel functionalities has led, over the past several years, to the use of colloidal templates as self-assembled building blocks for the fabrication of quasi-ordered sub-micron structures of various materials [1-4]. This approach has attracted a great deal of attention especially for the fabrication of photonic crystals but also as a means of synthesizing advanced catalysts and chemical sensors. It has been difficult, however, to employ this method to synthesize complex compounds and to ensure high reproducibility and throughput, largely due to the nature of the wet chemistry routes used to infiltrate the voids between the colloids with the precursors [5,6]. In this work we demonstrate successful application of microsphere templating to the fabrication of macroporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and TiO_2 films via pulsed laser deposition (PLD) onto poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) templated substrates.

PLD is a versatile thin film deposition technique, well-known for its ability to transfer complex compositions of different classes of materials, such as high-temperature superconductors and ferroelectric materials, from the target onto the substrate [7]. As demonstrated in this work, the combination of chemical and physical synthesis routes benefits from the unique advantages of the respective methods, i.e., the self assembly feature provided by the organic microspheres enabling production of quasi-ordered templates with sub-micron dimensions, and the deposition of thin films and multilayer structures with precisely and reproducibly controlled properties via physical vapor deposition (PVD). Upon subsequent removal of the organic template by thermal decomposition, the residual deposited inorganic film exhibits a macroporous structure with large surface area and surface to volume ratio. Consequently, its gas sensitivity can be expected to be markedly improved with respect to similar films deposited on untreated substrates as demonstrated in the following.

2 EXPERIMENTAL

The scheme in Figure 1 illustrates the procedure used in this study to fabricate the macroporous CCTO films. An aqueous suspension (2 wt. %) of 800 nm PMMA microspheres (Soken Chemical & Engineering Co., Tokyo, Japan), ultrasonically dispersed in deionized water, was dripped by pipette onto Al_2O_3 substrates with interdigitated Pt electrode arrays (200 μm Pt fingers spaced 200 μm apart), and dried overnight in a desiccator at room temperature. CCTO films were deposited by PLD onto the microsphere templated substrates, as well as onto untreated substrates for comparison purposes, from a $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ target prepared by a conventional solid-state reaction method using high purity CaCO_3 (99.99%), CuO (99.9%), and TiO_2 (99.99%) powders (Sigma-Aldrich Co., Milwaukee, USA). The powders were mixed at the stoichiometric ratio, milled for 24 h, calcined at 900°C for 11 h, and then pressed into pellets that were sintered in a tube furnace at 1100°C in air for 24 h. PLD deposition was carried out at ambient temperature and oxygen pressure of 4 Pa. Laser ablation was carried out at a fluency of 2.5 J/cm^2 and a repetition rate of 25 Hz using a KrF excimer source ($\lambda = 248 \text{ nm}$). Following the PLD deposition, the samples

were calcined in air at 800°C for 2 h to remove the PMMA microspheres. A similar approach was taken to synthesize macroporous TiO₂ films using 1.6 μm PS microspheres. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were used to examine the phase composition and microstructure of the films, respectively.

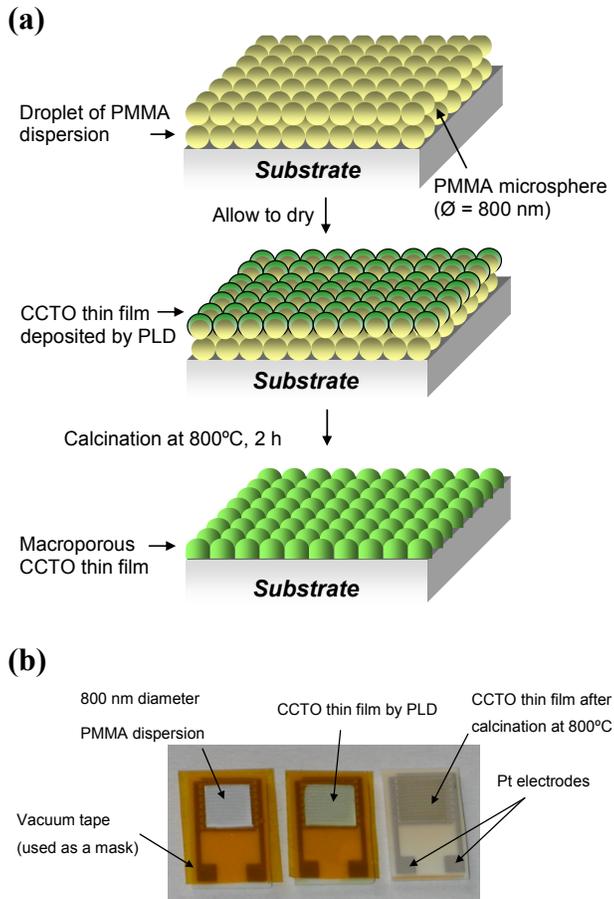


Figure 1: (a) Schematic diagram of the processing method used to fabricate macroporous CCTO films on Al₂O₃ substrates with interdigitated Pt electrode arrays. (b) Optical micrographs of gas sensor test devices (10 mm × 15 mm) with macroporous CCTO films. Reprinted with permission from Ref. [8]. Copyright (2006) American Chemical Society.

The sensitivity of the macroporous films towards H₂, CO, CH₄ and NO₂ gases was tested at temperatures between 200 and 400°C, and compared with similar films deposited on untreated substrates. Both templated and untemplated (control) films were deposited, calcined, and tested under the same conditions. They were mounted on Al₂O₃ sample holders and contacted by Pt wires which were attached to the interdigitated electrode arrays on the Al₂O₃ substrates using silver paste (SPI Silver Paste Plus, SPI Supplies, Chester, PA, USA). The sample holders were then inserted

inside a quartz tube placed in a tube furnace (Lindberg/Blue Model M 0.8 KW Tube Furnace). Pt/Pt-Rh (type S) thermocouples were used to measure temperature in-situ. The resistances of the templated and untemplated (control) films were measured in parallel during exposure to different gas compositions using bottled gases of dry air, 1000 ppm H₂ in air, 1000 ppm CO in air, 1% CH₄ in air, and 100 ppm NO₂ in air (BOC Gases, Riverton, New Jersey), together with mass flow controllers (Tylan UFC-1500A mass flow controllers and a Tylan RO-28 controller). To eliminate interfering effects due to changes in gas flow rate, the gas sensing tests were carried out at a constant flow rate of 200 sccm. The flow rate ratio of the carrier gas (dry air) and test gas (H₂, CO, CH₄, or NO₂ mixed in air) was varied between 1:0 (200:0 sccm) to 0:1 (0:200 sccm) in order to modulate the concentration of the test gas between 0 to 100% of the gas concentration in the pre-mixed gas bottle. The resistance was measured under a DC bias voltage of 0.1 V using 4-channel DC power supply and ammeter (HP 6626A and 4349B, respectively).

3 RESULTS

Figure 2 shows SEM micrographs of templated CCTO and TiO₂ films after the calcination step. The resultant films consisted of a monolayer of hollow hemispheres with diameter commensurate with the diameter of the PMMA or PS microspheres (0.8 and 1.6 μm, respectively). The hemisphere diameter can be easily controlled by selecting microspheres of different sizes. The wall thickness of the hemispheres was ~80-90 nm and the grain size varied between ~60 and 110 nm (cf. Fig. 2 a). These parameters can be controlled by adjusting the PLD deposition conditions and post-deposition calcination conditions. We note that size effects of the polymer microspheres on the pore size distribution, specific surface area, gas response kinetics, sensitivity and selectivity between different gases were systematically investigated by Hyodo et al. using 150, 250, 400, and 800 nm PMMA microspheres [9].

A network of voids between the film and substrate, as seen in Figure 2 (a), provides easy accesses of the gas phase to the internal surfaces of the hemispheres. These voids (“burst holes”) were formed, most likely, as a result of the microsphere decomposition during the calcination step. Consequently, the specific surface area is at least twice as large (top and bottom surface) and the surface area four times as large (top and bottom surface plus the geometric effect of the hemispheres) as in films deposited on planar untreated substrates. This unique morphology is expected to enhance their chemical activity and, at the same time, mitigate deleterious interfacial effects between film and substrate. Both effects are highly advantageous for gas sensors. On one hand, since the gas sensitivity is proportional to the specific surface area [10], one wants to reduce the critical dimensions of the sensing material (i.e., the grain size in case of porous ceramic layers of partially sintered grains or the film thickness in case of dense thin

films [11]) well below the 100 nm range. On the other hand, film/substrate interactions become increasingly important and the interfacial charge at the film/substrate interface adversely interferes with the surface interactions between the sensing film and the gas phase at such critical film dimensions, which often counteract the beneficial effects of reducing the film thickness to nanoscale dimensions. Thus, a synthesis strategy that enhances the surface area while, at the same time, reduces the interface area between film and substrate provides a unique solution to this dilemma.

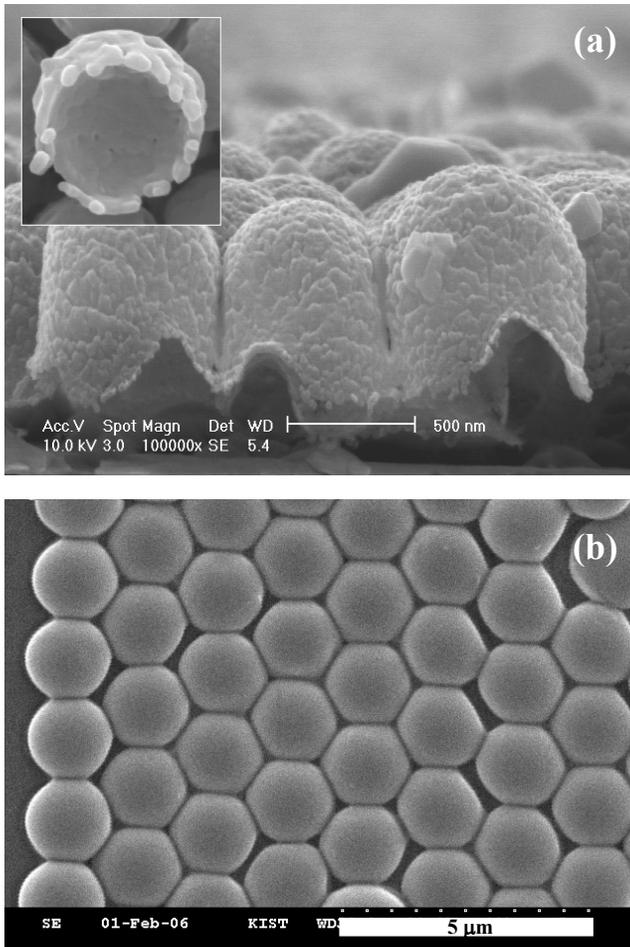


Figure 2: SEM micrographs of macroporous CCTO (a) and TiO₂ (b) films following calcination at 800°C. The inset in (a) emphasizes the grain structure of the hemispheres.

Figure 3 shows the resistance responses of macroporous (templated) and plain (untemplated) CCTO films upon exposure to increasing concentrations of H₂ in air (between 100 and 1000 ppm) at T = 300°C. The templated films were found to be quite sensitive to H₂, whereas the sensitivity of the control films deposited on untreated substrates was negligible. The remarkably enhanced sensitivity of the templated CCTO films is attributed to their macroporous structure (cf. Figure 2 a) with the high surface area promoting interactions with the gas and the

relatively small interfacial area mitigating the deleterious effects between film and substrate, as discussed above.

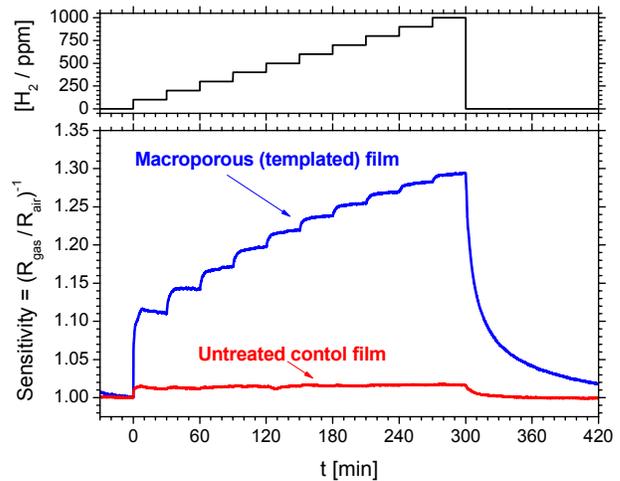


Figure 3: The resistance response of CCTO films deposited on templated (blue curve) and plain substrates (red curve) during exposure to increasing concentrations (between 100 and 1000 ppm) of H₂ in air at T = 300°C. Reprinted with permission from Ref. [8]. Copyright (2006) American Chemical Society.

Unlike H₂, the response of the macroporous CCTO films towards CO and CH₄ gases was negligible, as shown in Fig. 4. The reasons for the depressed sensitivities to these gases are unknown at present, although it may be related to carbon deposition at the surface which blocks the active surface sites. It is noted though that the selectivity of the CCTO films towards H₂ might be advantageous in applications where H₂ is to be selectively detected in gas atmospheres that may also contain interfering gases such as CO and CH₄.

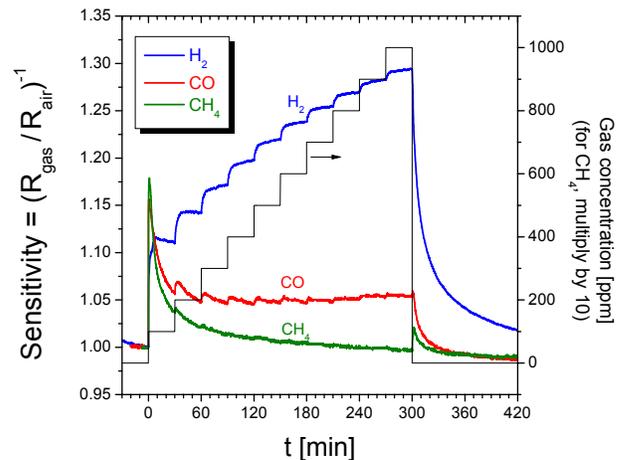


Figure 4: The resistance response of the macroporous CCTO films during exposure to increasing concentrations of H₂, CO, and CH₄ gases in air at T = 300°C.

4 SUMMARY AND CONCLUSIONS

Chemical and physical synthesis routes were combined to prepare macroporous $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and TiO_2 thin films by pulsed laser deposition onto polymer (PMMA or PS) microsphere templated substrates. The resultant films had a monolayer structure of quasi-ordered hollow hemispheres with high surface area, porosity, and permeability to gases. The enhanced surface area and reduced interface area between film and substrate provided by this synthesis method, as demonstrated in this work, leads to remarkable enhancement of the gas sensitivity of templated versus untemplated films. As such, this approach may lead to a breakthrough in thin film gas sensor technology, which holds notable advantages in terms of reproducibility and compatibility with microfabrication process compared to thick film process such as screen printing and spraying. Furthermore, this processing strategy can provide a simple yet versatile means to produce macroporous films of a wide variety of materials, especially inorganic materials, with ability to control parameters such as porosity, film thickness, composition, etc., as well as the ability to produce multilayer structures of compounds with complex chemistry. The ability to control the macroporous structure of such films on different length scales from some tens of nanometers up to several microns also enables systematic investigation of microstructure-property correlations in different classes of materials.

ACKNOWLEDGMENT

This work was supported, in part, by the National Science Foundation under contract #ECS-0428696. The authors thank Dr. Hyun Jung Lee for assistance with sample preparation.

REFERENCES

- [1] O. D. Velev, T. A. Jede, R. F. Lobo, and A. M. Lenhoff, *Nature* 389, 447, 1997.
- [2] B. T. Holland, C. F. Blanford, and A. Stein, *Science* 281, 538, 1998.
- [3] S. H. Park, and Y. Xia, *Adv. Mater.* 10, 1045, 1998.
- [4] M. Antonietti, B. Berton, C. Göltner, and H. P. Hentze, *Adv. Mater.* 10, 154, 1998.
- [5] A. Stein, and R. C. Schroden, *Curr. Opin. Solid State Mater. Sci.* 5, 553, 2001.
- [6] M. A. Carreon, and V. V. Guilants, *Eur. J. Inorg. Chem.* 27, 2005.
- [7] H. U. Krebs et al., *Adv. Solid State Phys.* 43, 505, 2003.
- [8] I.D. Kim, A. Rothschild, T. Hyodo, and H. L. Tuller, *Nano Lett.* 6, 193, 2006.

- [9] T. Hyodo, K. Sasahara, Y. Shimizu, and M. Egashira, *Sens. Actuators B* 106, 580, 2005.
- [10] A. Rothschild, and Y. Komem, *J. Appl. Phys.* 95, 6374, 2004.
- [11] N. Barsan, and U. Weimar, *J. Electroceramics* 7, 143, 2001.