

Applications of Atomic Layer Deposition of Tin Oxide

Sunny Aggarwal

Department of Chemical Engineering, City College of New York (CUNY)

NNIN REU Site: Penn State Nanofabrication Laboratory, The Pennsylvania State University, University Park, PA

NNIN REU Principal Investigator: Dr. Suzanne Mohney, Materials Science and Engineering, The Pennsylvania State University

NNIN REU Mentors: Haila Mohammed Aldosari and Shih-Ying Yu, MSE, The Pennsylvania State University

Contact: sunnygs94@yahoo.com, mohney@ems.psu.edu

Abstract:

Atomic layer deposition (ALD) produces high-quality, low-porosity conformal nanostructures. Tin dioxide, SnO_2 , is deposited within the void space of a face-centered cubic (FCC) silica opal lattice. SnO_2 is a viable metal oxide for the formation of inverse opals due to its stability when the silica spheres are etched away. Furthermore, we explore its use as an effective interfacial layer for ohmic contacts between a metal and semiconductor. SnO_2 is deposited by ALD using tetrakis (dimethyl amino) tin and water, then 30 nm sized opals are infiltrated with varying pulse lengths of these precursors in order to attain the most depth and complete infiltration. The resulting infiltrated SnO_2 opals are characterized through field emission scanning electron microscopy (FE-SEM) and the 4-point probe to explore its filling efficiency and resistivity differences. In this work, we fill opals that are smaller than those that have been previously studied.

Introduction:

Atomic layer deposition (ALD) is a modified chemical vapor deposition technique that provides conformal, uniform monolayer-by-monolayer growth. Such advantages allow for ALD to provide opportunities in optoelectronics [1] and microelectronics. An ALD cycle follows this process: dose with first precursor, tetrakis (dimethyl amino) tin (TDMASn); purge with N_2 gas to remove any excess reactants; dose with second precursor, water (H_2O); and finally purge the remaining reactants. In this study, ALD is used for infiltration of nano-opals and electrical contacts. Opals, 30 nm in size (smaller than those typically used for self-assembled photonic crystals) [2], were fabricated using the vertical deposition method. Self-assembly of these colloids created a face-centered cubic (FCC) lattice. Its 26% void space is infiltrated with tin oxide, SnO_2 , through ALD as shown by the half reactions discussed previously by Mullings, et al. [3].

SnO_2 is selected due to ability to make good electrical contacts. It is a wide band gap semiconductor that can have a high carrier concentration and that shows strong resistance towards a variety of etching agents, including HF, which is the sole reagent that the silica templates are etched away with. Also, aggressive scaling of devices calls for low contact resistance. The use of SnO_2 in contacts between a metal and a semiconductor are being explored. Such materials lower the effective Schottky barrier height, by relieving Fermi level pinning and lowering of the conduction band offset (CBO) [4].

Experimental Procedure:

Fabrication of Opals. Nano silica colloids are dispersed in an open vial solution. Inside it, silicon substrates are placed in at a diagonal of 45° . The solution is then evaporated in a drying oven for four days, slowly, allowing for the opals to self-assemble in the FCC lattice.

Preparation of Samples. One of the opal substrates was cleaved and degreased. Degreasing included the standard 3-step procedure: sonication in acetone for five minutes, followed by sonication in isopropanol for five minutes, and a final sonication in deionized water for five minutes. The sample was then blown dry with N_2 gas for 1-2 seconds and placed in a sterile sample holder.

ALD Recipes. The prepared samples were placed in an ALD reactor (Cambridge Savannah) set at these control conditions:

- Temperature of 150°C .
- N_2 purge flow rate of 20 sccm.

Conformal deposition of SnO_2 thin films utilized saturated pulse times of 0.030 s for TDMASn and 0.015 s for H_2O . The purge times were 30 s.

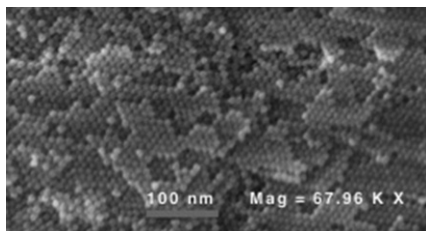


Figure 1: Empty opals; no dose of SnO₂.

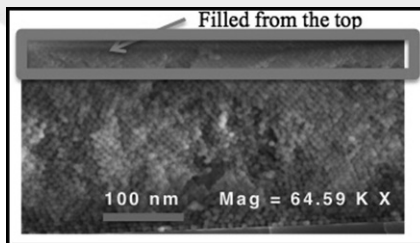


Figure 2: Infiltrated SnO₂ opal at a dose of 0.03 s of TDMASn and 0.015 s of H₂O.

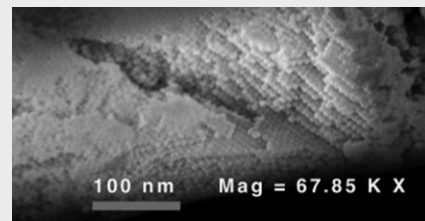


Figure 3: Infiltrated SnO₂ opal at a dose of 0.090 s of TDMASn and 0.045 s of H₂O.

Results and Conclusions:

Ellipsometry revealed that the growth rate of these films was $\sim 0.5 \text{ \AA/cycle}$. Since 5-6 nm of holes are to be filled from these 30 nm sized opals, 125 ALD cycles was used.

Figure 1 shows a FESEM image of the empty silica opal lattice, while Figure 2 demonstrates a partial filling of the opal from the saturated pulse times of the precursors. Hence, tripling the pulse times of each precursor respectively yields an almost complete infiltration as shown in Figure 3.

Further characterization of the opals done by the Keithley 2400 source-measure unit yields a variety of film sheet resistances, as shown in Figure 4.

Portrayed through the FESEM and data from the resistivity measurements, SnO₂ is shown to have deeper and a more complete infiltration into the opals as the dose increases. Such nano-scaled inverse opals can have applications in lithium ion batteries and gas sensors.

Future Works:

The silica template must be etched using ion milling (primarily to expose) and then a dilute aqueous HF solution to attain the SnO₂ inverse opals. Further characterization of these samples, such as by transmission electron microscopy, and measurement of their electronic properties can be further performed, and their applicability for batteries and sensors can be explored.

Acknowledgements:

The author thanks the support of Dr. Suzanne Mohny's lab group along with the nanofabrication staff in the Materials Research Institute of Pennsylvania State University and National Science Foundation for funding the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program.

Empty opals	
Average Voltage Measured (mV)	0.33
Current Used (nA)	5.0
Calculated Sheet Resistance (Ω)	66,000
SnO ₂ Opals with 60 cycles at a dose of 0.030 s of TDMASn and 0.015 s of H ₂ O	
Average Voltage Measured (mV)	0.11
Current Used (nA)	5.0
Calculated Sheet Resistance (Ω)	96,100
SnO ₂ on regular Si wafer at 150°C	
Average Voltage Measured (mV)	0.18
Current Used (nA)	1.0
Calculated Sheet Resistance (Ω)	829,000

Figure 4: Resistance Measurements.

References:

- [1] Niinistö, L., Nieminen, M., Päiväsaari, J., Niinistö, J., Putkonen, M. and Nieminen, M. "Advanced electronic and optoelectronic materials by Atomic Layer Deposition: An overview with special emphasis on recent progress in processing of high-k dielectrics and other oxide materials." *physics status solidi (a)* 201.7 (2004): 1443-1452.
- [2] Nishijima, Y., Ueno, K., Juodkazis, S., Mizeikis, V., Misawa, H., Tanimura, T., and Maeda, K. "Inverse silica opal photonic crystals for optical sensing applications." *Optics Express* 15.20 (2007): 12979-12988.
- [3] Mullings, Marja N. and Hägglund, Carl and Bent, Stacey F. Tin oxide atomic layer deposition from tetrakis (dimethyl amino) tin and water. *Journal of Vacuum Science & Technology A*, 31, 061503 (2013).
- [4] Yuan, Z., Nainani, A., Sun, Y., Lin, J. Y. J., Pianetta, P., and Saraswat, K. C. "Schottky barrier height reduction for metal/n-GaSb contact by inserting TiO₂ interfacial layer with low tunneling resistance." *Applied Physics Letters* 98.17 (2011): 172106.

M
A
T
S