Atomic Layer Deposition of Uniform Metal Coatings on Highly Porous Aerogel Substrates

Theodore F. Baumann,*,† Juergen Biener,†
Yinmin M. Wang,† Sergei O. Kucheyev,† Erik J. Nelson,†
Joe H. Satcher, Jr.,† Jeffrey W. Elam,‡
Michael J. Pellin,‡ and Alex V. Hamza†

Lawrence Livermore National Laboratory, Chemistry and Material Science Directorate, Livermore, California 94551, and Argonne National Laboratory, Energy Systems Division, Argonne, Illinois 60439

Received July 26, 2006
Revised Manuscript Received October 11, 2006

The design of nanoporous metals is currently an active area of research because materials of this type hold technological promise for a wide range of applications, including catalysis, energy storage and conversion, sensors/detectors, and nanoelectronics.[1−4] Traditional methods for the fabrication of nanoporous metals involve either a "bottom-up" approach,[5,6] such as aggregation of metal nanoparticles, or "top-down" techniques, such as dealloying.[7−10] These methods, however, offer limited control over composition and morphology of the resulting structure. A powerful method for controlling pore sizes and densities in cellular materials is the template approach.[11−15] In this technique, the template serves as the central framework that imparts the desired structural features to the material under construction. Depending on the type of template used, cellular materials with pore sizes ranging from micrometers down to a few Angstroms can be prepared. This templating approach has been used to fabricate metallic foams with a wide range of cell sizes.[16−24] Infusion of metal or metal precursors into a nanocellular template, however, is limited by the extremely high aspect ratios of the template pore structure, leading to inhomogeneous or incomplete coating of the template.

To overcome this limitation, we are developing a new templating method that utilizes aerogels and atomic layer deposition (ALD) for the fabrication of porous metal nanostructures. Aerogels are a special class of low-density, open-cell foams with submicrometer architectures,[25,26] and as such, are ideal templates for the preparation of nanocellular metal foams. Infusion of metals into these templates is accomplished by ALD, a process that provides atomic layer control of thin film growth through sequential, self-limiting surface reactions.[27] Because film growth is self-limiting for each deposition cycle, the ALD process can be used to deposit conformal films inside high aspect ratio structures.[28−31] With this approach, the properties of the resulting metal foam, such as porosity and density, can be reliably controlled through the selection of aerogel template and the number of metal deposition cycles. In this communication, we use ALD to deposit uniform tungsten (W) metal coatings on the skeletal network of two low-density metal oxide aerogel templates with different morphologies.

The two aerogels selected as templates for W ALD are representative of the range of nanostructures (i.e., surface area, nanoparticle morphology, porosity) available in these materials. The structure of the low-density alumina aerogels (60 mg/cc), prepared as boehmite (AlOOH), is comprised of nanoleaflets, 10−15 nm wide and more than 100 nm long, that interconnect to form a weblike microstructure (Figure 1a).[32] As a result, this material possesses a high specific surface area (∼700 m^2/g) and small pore diameters. Conversely, the low-density amorphous germania aerogels (35 mg/cc) consists of larger elongated nanorods, ∼20 nm in diameter and ∼50−200 nm in length, giving the material much lower surface area (∼60 m^2/g) and more open porosity (Figure 1c).[33] Tungsten was selected for deposition on these templates because the nucleation and growth of W metal films

---

* Corresponding author. E-mail: baumann2@llnl.gov.
† Lawerence Livermore National Laboratory.
‡ Argonne National Laboratory.

(1) Weissmüller, J.; Viswanath, R. N.; Kramer, D.; Zimmer, P.; Würschum, R.; Gleiter, H. *Science* **2003**, *300*, 312.
(2) Chan, S.; Kwon, S.; Koo, T. W.; Lee, L. P.; Berlin, A. A. *Adv. Mater.* **2003**, *15*, 1595.
(3) Kramer, D.; Viswanath, R. N.; Weissmüller, J. *Nano Lett.* **2004**, *4*, 793.
(4) He, X.; Antonelli, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 214.
(5) Velev, O. D.; Tessier, P. M.; Lenoff, A. M.; Kaler, E. W. *Nature* **1999**, *401*, 548.
(6) Jiang, P.; Cizeron, J.; Bertone, J. F.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 7957.
(7) Ding, Y.; Erlenbacher, J. *J. Am. Chem. Soc.* **2003**, *125*, 7772.
(8) Erlenbacher, J.; Aziz, M. J.; Karma, A.; Dimitrov, N.; Sieradzki, K. *Nature* **2001**, *410*, 450.
(9) Pugh, D. V.; Dursun, A.; Corcoran, S. G. *J. Mater. Res.* **2003**, *18*, 2166.
(10) Sun, L.; Chien, C. L.; Searson, P. C. *Chem. Mater.* **2004**, *166*, 3125.
(11) Zhao, X. S.; Su, F.; Yan, Q.; Guo, W.; Bao, X. Y.; Lv, L.; Zhou, Z. *J. Mater. Chem.* **2006**, *16*, 637.
(12) Stein, A. *Adv. Mater.* **2003**, *15*, 763.
(13) Schüth, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3604.
(14) Davis, M. *Nature* **2002**, *417*, 813.
(15) Huczko, A. *Appl. Phys. A* **2000**, *70*, 365.
(16) Ashby, M. F.; Evans, A. G.; Fleck, N. A.; Gibson, L. J.; Hutchinson, J. W.; Wadley, H. N. G. *Metal Foams: A Design Guide*; Butterworth-Heinemann: Boston, 2000.
(17) Banhart, J. *Prog. Mater. Sci.* **2001**, *46*, 559.
(18) Walsh, D.; Arcelli, L.; Ikoma, T.; Tanaka, J.; Mann, S. *Nat. Mater.* **2003**, *2*, 386.
(19) Xu, H.; Goedel, W. A. *Small* **2005**, *1*, 808.
(20) Shin, H. C.; Dong, J.; Liu, M. *Adv. Mater.* **2003**, *15*, 1610.
(21) Lei, Y.; Chim, W. K.; Zhang, Z.; Zhou, T.; Zhang, L.; Meng, G.; Phillipp, F. *Chem. Phys. Lett.* **2003**, *380*, 313.
(22) Brothers, A. H.; Dunand, D. C. *Adv. Mater.* **2005**, *17*, 484.
(23) Bartlett, P. N.; Baumberg, J. J.; Birkin, P. R.; Ghanem, M. A.; Netti, M. C. *Chem. Mater.* **2002**, *14*, 2199.
(24) Bartlett, P. N.; Marwan, J. *Chem. Mater.* **2003**, *15*, 2962.
(25) Baumann, T. F.; Gash, A. E.; Fox, G. A.; Satcher, J. H.; Hrubesh, L. W. In *Handbook of Porous Solids*; Schuth, F., Sing, K. S., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 2002; p 2014.
(26) Pierre, A. C.; Pajonk, G. M. *Chem. Rev.* **2002**, *102*, 4243.
(27) Leskalä, M.; Ritala, M. *Thin Solid Films* **2002**, *409*, 138.
(28) Kucheyev, S. O.; Biener, J.; Wang, Y. M.; Baumann, T. F.; Satcher, J. H.; Wu, K. J.; van Buuren, T.; Hamza, A. V.; Elam, J. W.; Pellin, M. J. *Appl. Phys. Lett.* **2005**, *86*, 083108.
(29) Pellin, M. J.; Stair, P. C.; Xiong, G.; Elam, J. W.; Birrell, J.; Curtiss, L.; George, S. M.; Han, C. Y.; Iton, L.; Kung, H.; Kung, M.; Wang, H. H. *Catal. Lett.* **2005**, *102*, 127.
(30) Chen, P.; Mitsui, T.; Farmer, D. B.; Golovchenko, J.; Gordon, R. G.; Branton, D. *Nano Lett.* **2004**, *4*, 1333.
(31) Rugge, A.; Becker, J. S.; Gordon, R. G.; Tolbert, S. H. *Nano Lett.* **2003**, *3*, 1293.
(32) Baumann, T. F.; Gash, A. E.; Chinn, S. C.; Sawvel, A. M.; Maxwell, R. S.; Satcher, J. H. *Chem. Mater.* **2005**, *17*, 395.

10.1021/cm061752g CCC: $33.50

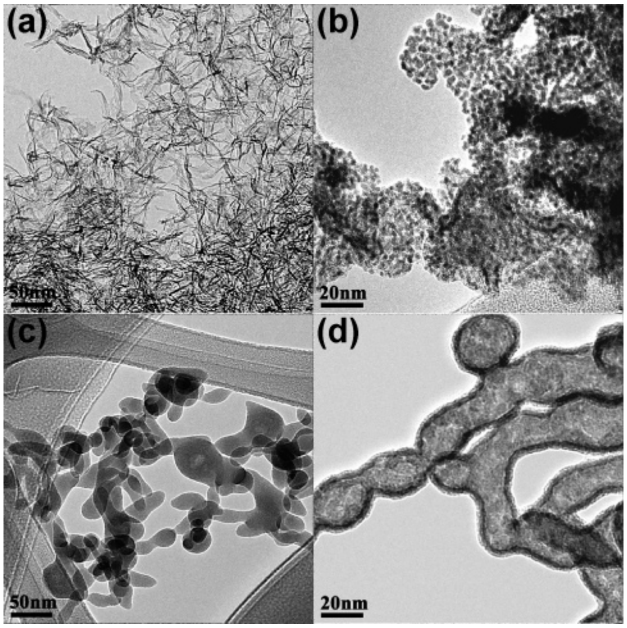

Figure 1. Bright-field transmission electron micrographs of the (a) uncoated and (b) W-coated alumina aerogel (6 ALD cycles), and the (c) uncoated and (b) W-coated germania aerogel (6 ALD cycles).

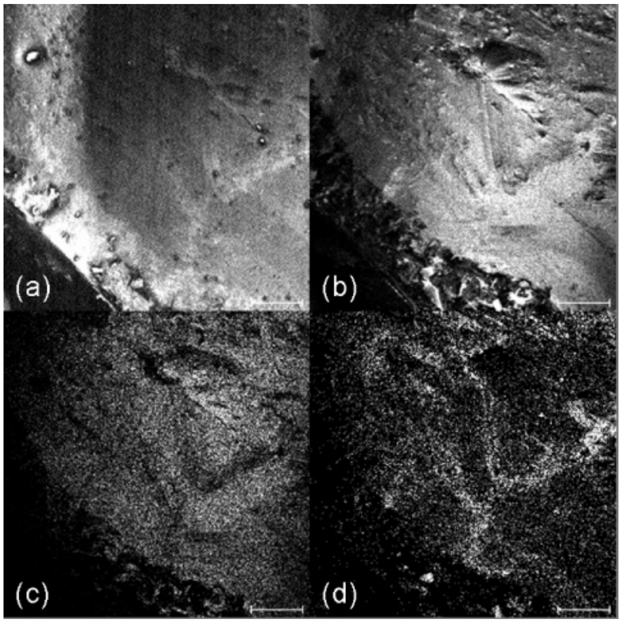

Figure 2. TOF−SIMS images of a fractured W-coated alumina aerogel (6 ALD cycles) formed by the following SIMS channels: (a) secondary electron, (b) total positive ion, (c) WO^+ ions, and (d) Al^+ ions (scale bar = 100 μm).

on flat surfaces by ALD has been extensively studied.[34−36] Atomic layer deposition of W metal is achieved by dividing the binary chemical vapor deposition reaction $WF_6(g) + Si_2H_6(g) \rightarrow W(s) + 2SiHF_3(g) + 2H_2(g)$ into two separate self-limiting half reactions. Exposure of a substrate to alternating cycles of disilane (Si_2H_6) and tungsten hexafluoride (WF_6) at elevated temperatures leads to atomic layer growth of W metal films at a rate of ∼2.6−5.2 Å/cycle. To ensure that these precursors fully penetrate the aerogel network, exposure times had to be increased significantly relative to cycle times used for ALD on flat surfaces. In a typical reaction (or AB) cycle, an aerogel monolith (a few mm^3 in size) was treated with alternating 600 s exposures of Si_2H_6 and WF_6 at 200 °C with 300 s purges between each half reaction.[37] For the germania aerogel, a protective aluminum oxide layer was deposited prior to exposure to W ALD to prevent etching of the aerogel by the WF_6 precursor.[38] The first few W ALD cycles did not yield significant mass gain for either aerogel template. This observation was not unexpected, because the W ALD reaction typically requires several AB cycles to initiate W nucleation on a substrate. As a result, the film growth rate is not linear during this induction period, but becomes more uniform as the number of exposure cycles increase. For our materials, this induction period was typically three AB cycles, after which substantial weight gains (more than 2000% for 6 AB cycles) were measured for both types of templates.

The spatial and depth uniformity of the deposited W metal was investigated with time-of-flight secondary ion mass spectrometry (TOF−SIMS). In both materials, the W coatings are uniform throughout the entire aerogel monolith, as shown in the TOF−SIMS images of the alumina aerogel treated with 6 AB cycles (Figure 2). This result indicates that the longer exposure times were effective in allowing diffusion of the W precursors through the tortuous porosity of the aerogel template. The morphologies of the aerogels treated with six W ALD cycles were evaluated using high-resolution transmission electron microscopy (HRTEM). As shown in Figure 1, the overall microstructures of the aerogels are retained after ALD treatment and the deposition of tungsten is clearly evident on the surfaces of the skeletal aerogel networks. The morphologies of the deposited W metal, however, are quite different for the two templates. For the alumina aerogel, the coating consists of crystalline W nanoparticles, ∼2 nm in diameter, uniformly deposited on the surfaces of the nanoleaflets (Figure 1b). The nanorods of the germania aerogel, by contrast, are coated with a smooth conformal W film, ∼2 nm thick (Figure 1d). Because nucleation and growth of metal films by ALD depends critically on the uniformity of the substrate surface, this difference is likely related to the unique surface chemistry of each template. For the germania aerogel, the protective aluminum oxide layer that was deposited prior to W ALD creates an uniform surface for deposition. This uniformity results in high nucleation density of W metal on the aerogel surface, leading to conformal film growth. The surfaces of the alumina aerogels, however, were not treated prior to W deposition, leading to lower nucleation density of W on the alumina aerogels and the formation of discrete W nanoparticles. This ability to control the morphology of the deposited metal, either as nanoparticles or films, through the surface

---

(33) Kucheyev, S. O.; Baumann, T. F.; Wang, Y. M.; van Buuren, T.; Poco, J. F.; Satcher, J. H.; Hamza, A. V. *Appl. Phys. Lett.* **2006**, *88*, 103117.

(34) Fabreguette, F. H.; Sechrist, Z. A.; Elam, J. W.; George, S. M. *Thin Solid Films* **2005**, *488*, 103.

(35) Grubbs, R. K.; Nelson, C. E.; Steinmetz, N. J.; George, S. M. *Thin Solid Films* **2004**, *467*, 16.

(36) Elam, J. W.; Nelson, C. E.; Grubbs, R. K.; George, S. M. *Surf. Sci.* **2001**, *479*, 121.

(37) Atomic layer deposition was performed in a viscous flow reactor operated in a quasistatic mode at Argonne National Laboratory. Between each exposure, the reactor was evacuated below 0.24 Torr and then purged with ultrahigh purity N_2 for 300 s.

(38) The protective aluminum oxide layer was deposited on the germania aerogel through two alternating 600 s exposure cycles to trimethyl aluminum (5 Torr) and water (5 Torr) at 200 °C.

chemistry of the template can be a powerful tool in the design of new porous metal nanostructures.

The composition of the W coatings was examined by X-ray photoelectron spectroscopy (XPS). The W4f XPS spectrum for metallic W has two characteristic peaks at 31.2 eV (W4f$_{7/2}$) and 33.4 eV (W4f$_{5/2}$) with a small shoulder at 37.1 eV that is associated with the W5p electrons.[39] In the W4f XPS spectrum for WO_3, the most stable oxide of tungsten at room temperature, these two peaks are centered at 35.6 and 37.7 eV. The W4f spectra for the aerogels treated with six W ALD cycles shows four peaks that can be attributed to both metallic W as well as W^{6+} (Figure 3).[40] This result is consistent with the fact that the top surface of the deposited tungsten metal film oxidizes upon exposure to air. On the basis of the deposition rate for the W ALD reaction (2.6−5.2 Å/cycle) and the typical thickness of the native oxide layer for tungsten (∼10 Å), it is not surprising that the aerogels treated with 3 and 4 AB cycles exhibit W4f XPS spectra that correspond only to WO_3. Nevertheless, the native oxide layer on the surfaces of the thicker films can be removed through treatment with a hydrogen plasma and are not expected to have adverse effects on the fabrication of high-quality nanoporous metal structures.

In summary, this report details a new templating method for the preparation of porous metal nanostructures. This process utilizes ALD as a means for depositing conformal metal films on the inner surfaces of low-density aerogel templates. As a first example of the utility of this technique, we have presented the preparation and characterization of W-coated alumina and germania aerogels. Microstructural analysis of these materials shows that W deposition is uniform throughout each template and that the morphology of the deposited metal, either nanoparticle or film, depends on the surface chemistry of the skeletal aerogel network. As metal ALD techniques continue to mature, the approach presented here could be extended to a wide range of metals and templates, allowing for the design of metal nanostructures with controlled porosities and densities.

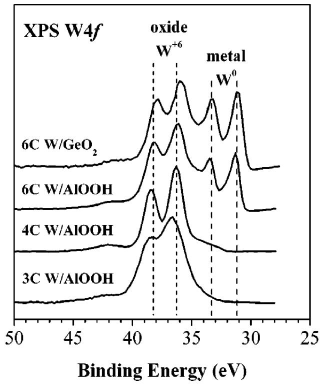

Figure 3. Tungsten 4f XPS spectra for the W-coated germania (6 ALD cycles) and alumina aerogels (3, 4, and 6 ALD cycles).

Acknowledgment. Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

CM061752G

---

(39) Warren, A.; Nylund, A.; Olefjord, I. *Int. J. Refractory Metals Hard Mater.* **1996**, *14*, 345.

(40) The XPS data have been background subtracted, normalized, and charge corrected using the C1s peak at 284.8 eV as the internal standard.