Cover Photo:
Photograph of 100 micron thick, hollow, nano-to-microcrystalline diamond capsules.

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Auspices Statement
This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.
Mission Statement: The Nanoscale Synthesis and Characterization Laboratory’s (NSCL) primary mission is to create and advance interdisciplinary research and development opportunities in nanoscience and technology.

The initial emphasis of the NSCL has been on development of scientific solutions in support of target fabrication for the NIF laser and other stockpile stewardship experimental platforms. Particular emphasis has been placed on the design and development of innovative new materials and structures for use in these targets. Projects range from the development of new high strength nanocrystalline alloys to graded density materials to high Z nanoporous structures. The NSCL also has a mission to recruit and train personnel for Lab programs such as the National Ignition Facility (NIF), Defense and Nuclear Technologies (DNT), and Non-proliferation, Arms control and International security (NAI). The NSCL continues to attract talented scientists to the Laboratory. Monika Biener from Harvard University’s Center for Mesoscale Characterization, Luis Zepeda-Ruiz from Princeton University, and Joel Hayes from Arizona State University joined the NSCL this year.
The NSCL is pursuing four science and technology themes: nanoporous materials, advanced nanocrystalline materials, novel three-dimensional nanofabrication technologies, and non-destructive characterization at the mesoscale. The NSCL is also pursuing new science and technology through use of recent IGPE investments such as the focused ion beam facility and the x-ray microscope.

We continue to lead in the synthesis and characterization of nanoporous metals. We have discovered, developed, and refined an array of synthesis approaches for nanoporous metals with relative densities below 25% and pore sizes on the nanometer length scale. Nanomechanical characterization techniques have led to the exciting discovery of unusual high strength of nanoporous metals.

Another area of expertise is the development of advanced nanocrystalline materials synthesis. We have used electrodeposition and sputtering techniques to successfully synthesize nanocrystalline Au/Cu alloy and body-centered-cubic (BCC) Ta. Both of these materials exhibit excellent hardness and tensile strength properties. The deformation mechanisms of these materials with grain sizes of 10-20 nm and below are being addressed through molecular dynamics models.

Development of novel 3-D nanoscale fabrication techniques is the third main theme of the NSCL. We have established new tools for 3-D fabrication such as focused ion beam processing and proximity field nanopatterning.

Nondestructive, mesoscale characterization is the fourth main theme of the NSCL. We are establishing new tools in x-ray imaging and scattering techniques to provide nanoscale to microscale characterization.

**Highlights for FY05**

In FY05 we have made substantial progress in our four theme areas: nanoporous materials, advanced nanocrystalline materials, novel 3D fabrication and mesoscale characterization. Below is a summary of some of the highlights.

![Figure 1. MD simulations of nanocrystalline copper are shown. Slices of pure Cu (top) and Cu-2%Fe(bottom) after 5% deformation are depicted. Red indicates significant displacement from initial positions. Black dots are Fe atoms.](image)
Understanding the mechanisms that lead to enhanced strength of nanocrystalline metals is not yet mature. We have been interested in the role impurities play on the thermal and mechanical behavior of nanocrystalline metals. Figure 1 shows slices of molecular dynamics simulations of the deformation behavior of pure nanocrystalline copper and iron-doped nanocrystalline copper. The iron impurity segregates to the grain boundaries where it suppresses deformation.

This year has seen remarkable progress in the technology and science for diamond ablator capsules. In collaboration with the Fraunhofer Institute for Applied Solid State Physics we have developed techniques to coat 2 mm diameter silicon mandrels with plasma enhanced chemical vapor deposited diamond. We have grown 70-100 micron thick shells. The shells have been polished to sub 50 nm surface roughness. And the mandrel has been etched out of the shell through a sub 20 micron, pulsed-laser drilled hole. Figure 2 shows a photograph of one batch of these micro-nanograined diamond ablators, where one shell has been laser cut to view the interior of the capsule.

Another significant breakthrough this year was the synthesis of the lowest density nanoporous metals. We used two techniques to reach relative densities of 10% or less. The first was dealloying which had been thought to be limited to relative density of 20%. We broke this barrier by synthesizing a bimodal pore distribution through sequentially dealloying a ternary alloy (see figure 3.). The second method is atomic layer deposition on aerogel tempalates.

Figure 2. 100 micron thick nano-microcrystalline diamond capsules.

Figure 3: The bimodal pore structure resulting from dealloying process, with an intermediate anneal to coarsen the structure. The starting alloy was Cu_{70}Ag_{20}Au_{10}. The final Au monolith had 10% relative density.

An in situ technique is required to determine the degree to which nanoporous structures can be wet and how the structures change upon wetting with cryogenic liquids. Since no direct non-destructive imaging capability exists with nanometer scale resolution and millimeter field-of-view, we have explored the use of small angle x-ray scattering (SAXS) to measure the morphology of the solid ligaments and distribution of the nanopores (see figure 4). We are establishing SAXS as the technique to non-destructively probe pore structure in the sub-50 nm regime; it is in this nanometer regime that the chemical and structural properties of nanoporous materials are determined.
(e.g. wetting, nanomechanics, catalysis, and filtration).

Figure 4. Comparison of destructive (transmission electron micrograph, top) and non destructive evaluation (small angle x-ray scattering, bottom) of GeO₂ Aerogel (35 mg/cm³).

The final theme area of the NSCL is the novel use of 3D lithography. Figure 5 shows an example of the use of deep reactive ion etching of silicon through an oxide mask and then filling the etched structure with polymer. The cured polymer structure is released from the silicon structure by isotropic wet etching of the silicon.

Figure 5. Pyramidal density gradient structures formed in Photopolymer SU8.

Plans for FY06

For the coming fiscal year a major focus in the NSCL will be to continue to deliver on the strategic initiative, “Nanoscale Fabrication Science and Technology.” The strategic initiative focuses three of our themes of nanoporous materials synthesis, advanced high strength materials, and novel three-dimensional fabrication with a design coordination element led by Peter Amendt.

We will pursue progress in diamond science to ready the diamond ablator capsule technology for FY07 by developing a doping capability. Au/Cu capsule fabrication with strength and permeability will be a high priority for this coming year. We will concentrate our nanoporous metals effort on atomic layer deposition in FY06. In addition we are planning to establish an atomic layer deposition capability at LLNL. FY06 will also see increased efforts on advanced assembly.

The NSCL is also beginning new efforts in support of the transformation materials initiative (TMI). The first effort is focused on establishing a capability in strong ductile materials with nanoscale features and the second is focused on producing nanostructured polymers to combine functionality. This
approach offers controlled fabrication of nano-scale periodic structures. During FY06 we will continue our research on acoustic characterization of mesoscale objects. We also will be quantifying dimensional metrology information from radiographs and computed tomography data.

The NSCL is primarily funded by LDRD investments and Tech Base/Materials Technology Projects. Tables 1 and 2 show the investments for FY05 and planning for FY06 discussed above.

Table 1. LDRD Investment and Planning for the NSCL

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<tr>
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Table 2. G&A, IGPE, Materials Technology Projects and Tech Base Projects Investments and Planning in the NSCL

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<tr>
<td>Diamond CVD reactor</td>
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<td>Total</td>
<td>750K</td>
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# Nanoscale Synthesis and Characterization Laboratory
## Annual Report 2005

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We have been exploring the synthesis of and strengthening mechanisms in nanocrystalline materials. The materials we have been investigating are Au/Cu and Ta, as candidates for inner shell capsules in an ignition double shell. A second goal is hydrogen permeation of the inner shell without loss of strength. Hence we have actively pursued mechanisms for pinning grain boundaries in nanocrystalline materials.
The tensile strength of nanocrystalline Au/Cu alloys
Y.M. Wang, A.F. Jankowski, A.V. Hamza

Nanocrystalline Au/Cu foils with thickness values of 10-20 micrometers are successfully fabricated by electrodeposition. Characterization of nanostructures is accomplished by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Mechanical properties are assessed with uniaxial tensile testing. The measured tensile strength in several as-deposited foils yields values as high as ~860 MPa which is greater than the strength requirement (~500 MPa) for double-shell ignition targets. Vacuum anneal treatments at 225 ºC demonstrate that the Au/Cu nanostructures remain stable. These results are promising for the potential application of Au/Cu alloys in fusion target fabrication.

The successful fabrication of double-shell ignition capsules relies on the synthesis of high strength and thermally stable nanocrystalline Au/Cu alloys. Bulk Au/Cu alloys are traditionally soft materials with the strength <100 MPa that prevents them from holding several hundred atmospheric pressures of DT gas required for inertial confinement ignition. There are several processing paths to improve the strength of Au/Cu alloys. For example, the selection of an optimum alloy composition with thermal aging treatments can be used [1] to create high-strength ordered Au/Cu phases. Another independent path to strengthen the disordered alloy of any composition is by reaping the benefit of the Hall-Petch strengthening mechanism. The strength of Au/Cu alloys may be escalated by a factor as much as 5-6. Our previous Au/Cu electrodeposition work [2] has demonstrated that the Hall-Petch strengthening effect is observed wherein the Vickers microhardness is increased from 0.6 GPa to 2.9 GPa for 5 wt.%Cu nanocrystals with grain sizes of 6 nm (as estimated from x-ray peak broadening). These results, together with the electrodeposition capability developed in the LLNL deposition laboratories, provide the foundation for preparing specimens for the tensile strength measurements summarized here. Figure 1 shows a typical transmission electron microscopy (bright field) image of an as-deposited Au/Cu alloy with nanocrystalline grain sizes.

Figure 1. Transmission electron micrograph of an as-fabricated nanocrystalline Au/Cu alloys. The grain sizes revealed in the TEM is slightly larger than those computed through X-ray diffraction line-broadening technique.

One of the ultimate goals of this project is to develop nanocrystalline Au/Cu alloys with tensile strength greater than 500 MPa along with high thermal stability. Valuable information can be attained from tensile test experiments. However, there is a list of challenges involved in the tensile tests of nanocrystalline materials. An example is the successful removal of the Au/Cu foils from its electrode substrate without damaging the integrity of the deposits.
Bending or twisting makes foils ill-suited for tensile tests. A second problem is to have a large enough area of thin foils (often in centimeter dimensions) for machining large enough tensile specimens to ensure valid measurements. A third requirement is to guarantee high quality edges of the tensile samples, as tensile results are sensitive to edge flaws. A fourth issue for testing thin foils is that good alignment is essential to prevent premature tearing of the samples. To overcome these problems, we have developed a series of in-house techniques to handle normally small and fragile tensile samples. Fig. 2 displays the optical micrograph of a laser-cut nanocrystalline Au/Cu tensile sample, showing the smooth and flat surface, as well as sharp and straight edges. These features show the high quality of the tensile specimen.

Figure 2. Optical micrograph of the gauge section of a laser-cut Au/Cu tensile sample showing the smooth surface and nice straight edges suitable for tensile measurements.

The tensile-test fracture surfaces observed suggest that the as-synthesized nanocrystalline Au/Cu alloys are microscopically ductile. Dimple features are clearly visible in a typical SEM image (shown in Fig. 3). However, macroscopically, these nanocrystalline Au/Cu alloys exhibit little or no ductility. This result is consistent with the trend normally observed in other nanocrystalline materials. For example, the tensile ductility of nanocrystalline materials typically decreases with decreasing grain size.

Figure 3. Scanning electron micrograph of the fracture surface of Au/Cu samples. Ductile features such as dimples are visible.

Table I shows the tensile strength measurement results of several Au/Cu samples. Strength levels above ~400 MPa are routinely achieved with the highest value approaching ~860 MPa. Such impressive strength is above the targeted stress requirement for applications. Also, the stability of the Au/Cu nanocrystalline alloys has been investigated using vacuum anneal experiments. The tensile strength of several 225°C-annealed samples are measured and included in Table I. The general finding that the tensile strength of annealed samples remains or even slightly increases indicates thermal/mechanical stability for the Au/Cu nanostructures.

In summary, we have developed expertise to measure the tensile strength of free-standing nanocrystalline Au/Cu foils. These strength measurement results demonstrate that the
electrodeposited nanocrystalline Au/Cu has great potential for use as an inner-shell target material for double shell targets.

<table>
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<tr>
<th>Sample Set</th>
<th>as-deposited grain size (nm)</th>
<th>as-deposited strength (MPa)</th>
<th>225 °C anneal strength (MPa)</th>
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<tr>
<td>CG2</td>
<td>7.1</td>
<td>470±40</td>
<td>350</td>
</tr>
<tr>
<td>CG3</td>
<td>5.2</td>
<td>775±75</td>
<td>-</td>
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<tr>
<td>CG5</td>
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<td>490±20</td>
<td>750</td>
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<td>CG7</td>
<td>82.5</td>
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References

The electrodeposition of a gold-copper composition gradient
Alan F. Jankowski, James L. Ferreira, Nerine Cherepy, and Jeffrey P. Hayes

Abstract
High strength Au-Cu alloy coatings are an option for potential use in double-shell ignition-capsule designs. It’s well known that the reduction of grain size to the nanoscale increases the strength of metal alloys. The use of pulsed electrodeposition provides a path to produce nanocrystalline AuCu alloys. This process method is further developed to produce a concentration gradient through the thickness of the electrodeposit.

Introduction
A process method and grain growth model were recently developed to control and understand the role of deposition parameters on nanocrystalline formation in electrodeposits.[1] This work follows the long-standing technological interest that LLNL has in electroplating coatings.[2] The electrodeposition of gold-copper (Au-Cu) alloys with constituent grain sizes as small as 5 nm have been produced with failure strengths as high as 875 MPa in tension. The use of a composition gradient in the cross-section of a Au-Cu coating leads to the optimization of a double-shell ignition capsule. The role of current density in the electrodeposition process is well known to preferentially deposit metal ions from an electrolytic bath that contains more than one species.[3] The application to produce a controlled concentration gradient is now demonstrated for Au-Cu electrodeposits.

Method
Au-Cu alloy coatings are prepared through the aqueous process of plating metal ions using a solution formed from potassium cyanide salts of gold and copper, i.e. a variation of a No. 2 Au bath with a 11±0.5 pH.[1, 3-4] A pulsed electrical pulse is passed through the ionic solution from the anode to the working electrode surface where the metal coating forms. The metal-ion solution is placed within a 1.5-liter polypropylene tank that’s suspended within the water bath of a stainless steel tank. Convective heating of the water bath warms the metallic solution to a temperature of 60±5°C. An inert platinum (Pt) anode is used with a substrate cathode of titanium (Ti).

The gold composition (c Au) is determined using a scanning electron microscope by a semi-quantitative analysis of energy dispersive x-ray spectra. The x-ray spectra generated from an incident electron-beam probe reveal characteristic Cu L and Au M x-ray peaks that are used to quantify the composition of the foils.

Results
To define the current-voltage parameter space to produce Au-based coatings from cyanoalkaline solutions, according the standard reaction as represented in eqn (1), we perform a cyclic voltammetry measurement using a Luggin capillary.

\[
\text{Au(CN)}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{Au} + 2\text{HCN}
\]

The independent measurement of absolute anode and cathode potentials with respect to a Ag/AgCl reference electrode indicate that potentials below -1.5 V and above -0.3 V should be avoided, as seen in Fig. 1, to prevent inefficient use of current (and hydrogen...
gas evolution) as well as etching of the deposit (and oxygen generation).

Figure 1. The current density $j$ (mA·cm$^{-2}$) is measured as the cathode-to-anode potential $U$ (Volts) referenced to a Ag/AgCl electrode is cycled at 10 mV·sec$^{-1}$.

To produce a composition gradient, the average pulsed current ($i$) is varied to produce a controlled change in the electrochemical cell potential ($U$). We confirm, as seen in Fig. 2, that a decrease in the pulsed-current density ($j$) and hence, the average cell potential favors deposition of the more noble metal species.[1, 3]

Figure 2. The Au concentration $c_{Au}$ (wt.%) of the coating produced by electrodeposition from a cyanoalkaline solution varies with the average cell potential as induced through a pulsed-current density $j$ (mA·cm$^{-2}$).

Au-Cu foils up to 50 microns in thickness are fabricated by electrodeposition wherein the pulsed-current density is sequentially increased with time. To measure the composition gradient of samples, the high-voltage electron-beam probe is incrementally stepped across the coating as prepared in cross-section. A variation in composition from above 90 wt.% to less than 20 wt.% can be produced as seen in Fig. 3. The pulsed-current method accelerates deposition using a greater average-current density (seen in Fig. 2) than for a ‘continuous’ current condition (seen in Fig. 1).

Figure 3. The variation of Au concentration $c_{Au}$ (wt.%) through the thickness ($\mu$m) of the coating directly correlates to the average electrochemical-cell potential $U$ (Volts).

References

Modeling the Electrodeposition of Nanocrystalline Au-Cu
Alan F. Jankowski

Abstract
The process parameters of current density, pulse duration, and cell potential affect both the structure and composition of the foils. To develop an understanding of the role of the process parameters on grain size – as a structural design parameter to control strength, for example, a formulation is presented that models the affect of deposition energy on grain size.

Background
Coatings of gold-copper (Au-Cu) are prepared [1] through the process of pulsed electroplating operated in the galvanic mode. The current (i) and cell potential (U) are measured between an inert platinum anode and a cathode (sheet of titanium). A cyanoalkaline solution of Au with Cu is used where the bath has a pH of ~11 and is heated to a temperature of 55-75 °C. Coating morphology varies with process parameters from a smooth to nodular growth as the current density increases. The crystallite size within each foil is quantified using the Debye-Scherrer formulation for Bragg peak-broadening in x-ray diffraction scans obtained in the θ/2θ mode.

The grain size decreases inversely with an increase in the current density (j). A ln-scale plot of the charge density (j·tp) versus the grain size (dg), as seen in Fig. 1., best evidences this parametric relationship. Two regimes can be distinguished based on the duration of the on-time (tp) for the pulsed current. A short pulse (tp < 5 msec) shows a faster decrease in dg with increasing j than does the long pulse (10 < tp < 30 msec) regime. The use of a pulsed-current is well known to refine the dg of the electrodeposits. A pulsed current facilitates nuclei formation as the peak current density can be considerably higher than the limiting direct-current density. It’s observed that dg refinement at the nanoscale is enhanced for the Au-Cu electrodeposits at greater current densities as the pulse duration (tp) is decreased from 10-30 msec to < 5 msec. This result may suggest a difference in the barrier for stabilization of grain size between each pulse-duration mode. That is, the long pulse overcomes an additional barrier to inhibit bulk-like diffusion whereas growth for the short pulse is primarily limited to the energetic barriers for nucleation and surface diffusion. The long pulse mode should have a barrier (Qlp) for grain formation that is greater than the energy (Qsp) for the short pulse mode.

Figure 1. The variation of grain size dg (nm) with ln-scale of charge density j·tp (µC·cm⁻²) for short (t< 5 msec) and long (10< t< 30 msec) pulsed electrodeposition of Au-Cu.

Nanocrystalline Growth Model
A model [2] is developed to determine the activation energy (Q) for grain
formation. A classic Arrhenius-type behavior for temperature-dependent diffusion in solids is assumed for the condition of ideal grain growth, i.e. $d_g^2 \alpha t_p$. Diffusion is mitigated by a negative exponential of the activation energy ($Q$) relative to the deposition energy ($Q^*$), i.e. electric work. For electrodeposition, $Q^*$ is equivalently defined from Faraday’s Laws as the integral product of the cell potential ($U$) with the total charge ($q$) in the number ($n^*$) of deposited units, i.e. $n^*q^*$, during each pulse. Accordingly, $Q^*$ is proportional to $\frac{1}{2}N_A(n^*)^2q^*U$ where $N_A$ is the Avogadro number and $q^*$ is equal to the product of the average current density ($j$) with the unit surface area ($A^*$) divided by the number of atoms ($n_o$) within the area projection noting that $n_o$ equals two for face-centered-cubic metals. Thus, $Q^*$ can be reduced to the equivalence of $N_A(jt_pa_o^2)U$.

In the (Fig. 2.) plot of $(Q^*)^{-1}$ with $\ln[\delta(d_g^2t_p^{-1})]$, a straight line is found as anticipated – the slope of which is equivalent to $-Q$. An activation energy ($Q$) for grain formation in the long-pulse mode ($Q_{lp}$) equals 1.52 eV·atom$^{-1}$ whereas for the short-pulse mode ($Q_{sp}$) equals 0.16 eV·atom$^{-1}$. As first seen in the grain size variation with current density, there are two regimes for nanocrystalline growth – a short and long pulse mode, each with distinct activation energies. For comparison, a greater activation energy ($Q_t$) for grain growth of 1.85 eV·atom$^{-1}$ is reported in the literature for high-temperature tracer diffusion studies of Au$^{98}$ in both Au and Cu, i.e. $Q_{sp} < Q_{lp} < Q_t$ as anticipated.

![Figure 2. The natural logarithm of grain size $d_g^2$ squared (cm$^2$) divided by the pulse duration $t_p$ (sec$^{-1}$) yields an Arrhenius plot with the inverse of deposition energy $Q^*$ (mol·J$^{-1}$).](image)

**Summary**

An empirical model is developed to provide a relationship between the electrodeposition process parameters and the nanocrystalline grain size. The grain size ($d_g$) can be determined from the parameters of current density ($j$), on-pulse time ($t_p$), and cell potential ($U$). Regimes for nanocrystalline growth include a short- and long-pulse mode, each with distinct activation energies. The long pulse mode has the additional contribution of surface and bulk-like diffusion whereas the short pulse mode is primarily limited to nucleation.

**References**


We have developed the expertise to fabricate nanocrystalline tantalum with grain sizes smaller than 30 nm, using multilayer physical vapor deposition (PVD). The as-synthesized nanocrystalline tantalum is predominately in the tetragonal structure (beta-Ta) with foil thickness of ~1 µm and the Vickers hardness values of 16–22 GPa. Furthermore, the hardness of the fabricated materials is observed to decrease with increasing deformation strain rate (i.e. negative strain rate sensitivity). This suggests a pressure-induced phase transformation behavior in nanocrystalline tantalum. The results demonstrate that nanocrystalline tantalum is an interesting material to investigate and that it could have potential applications in inertial confinement fusion target fabrication.

Our previous work (in collaboration with UC Davis) [1,2] demonstrated that nanocrystalline tantalum with very high hardness values and grain sizes smaller than 20 nm can be produced through a PVD process. Note that tantalum has a melting temperature of more than 3000°C, therefore the thermal stability of these materials is of little concern, making it attractive for a variety of applications. The first goal of this work is to develop the capability to produce large scale nanocrystalline tantalum samples with high reproducibility, scalability, and well-controlled phase and microstructures. The second goal of this work is to gain in-depth knowledge about the mechanical behavior of the nanocrystalline tantalum.

Inspired by our recent success in the production of high purity and high strength nanostructured copper [3], we adapted the multilayer nanotechnology and deposited tantalum materials layer-by-layer using magnetron sputtering technique. The microstructures of the as-fabricated nanocrystalline tantalum are controlled by adjusting individual layer thickness. The layer-by-layer PVD process also helps to relax the high residual stress developed during Ta film deposition, which is one of the major obstacles preventing fabrication of large scale, high quality foils.

Depending on the chamber base-pressure, the substrate, and the deposition rate, nanocrystalline tantalum with different mixtures of alpha- and beta-phases was successfully fabricated, as determined by X-ray diffraction spectra shown in Fig. 1.

The mechanical response of the as-fabricated nanocrystalline tantalum was probed with a depth-sensing Tribo-nanoindenter. Fig. 2 shows a typical loading-unloading force-displacement curve of nanocrystalline tantalum at two different loading rates. The hardness and the Young’s modulus values were calculated using the unloading portion of the curves. It can be seen from Fig.2 that...
at the higher loading rate of 5000 µN/s, nanocrystalline tantalum shows a lower hardness value (~16GPa), compared with that of ~21GPa at the loading rate of 50 µN/s.

Fig. 2 Typical loading-unloading force-displacement curves of nanocrystalline tantalum at loading rates of 5000 µN/s and 50 µN/s, respectively. The unloading curves indicate that at higher loading rate, nanocrystalline tantalum behaviors more “softly”.

Fig. 3 summarizes the hardness value of beta-phase nanocrystalline tantalum tested at the loading rates ranging from 50µN/s to 50,000µN/s. Each hardness value is averaged from at least 20 measurements. A clear trend can be seen in Fig.3; the hardness value of nanocrystalline tantalum decreases with increasing loading rate, suggesting that nanocrystalline tantalum has a negative strain rate sensitivity behavior. This observation is counterintuitive to the observations of conventional and other nanocrystalline materials.

Interestingly, such negative strain rate sensitivity behavior was only observed in beta-phase nanocrystalline tantalum but not in alpha-phase ones. This leads us to believe that nanocrystalline Ta might have gone through beta to alpha phase transformation under the high pressure induced by the nanoindenter, as beta-tantalum has a higher hardness value compared with alpha-Ta. More conclusive evidence regarding such phase transformation behavior in nanocrystalline tantalum is needed in the future. Currently, we are carrying out high-pressure experiments and cross-sectional TEM examinations to confirm the occurrence of such transformations.

References
Atomistic simulations of grain boundary annealing and pinning in nanocrystalline CuFe alloys

George H. Gilmer, Luis A. Zepeda-Ruiz, Babak Sadigh, Alfredo Caro, Tomas Oppelstrup, and Alex V. Hamza

The mobility of grain boundaries (GB) is a crucial factor that determines the stability and strength of nanocrystalline materials [1-3]. In order to take advantage of restricted dislocation motion, it is essential to ensure a stable grain structure. We have applied a hybrid Monte Carlo-molecular dynamics code to the study of grain boundary motion during annealing of Cu containing low concentrations of Fe. The hybrid simulations account for segregation and precipitation of the low solubility Fe, together with curvature driven grain boundary motion. The direct application of our work is to the fabrication of NIF double shell targets, where the inner shell is composed of high-Z materials; e.g., AuCu. These targets must sustain annealing temperatures up to 500°C, and pressures of 800 atmospheres, for extended periods.

Early models of impurity drag are based on continuum descriptions of GB structure that tacitly assume either pinning of the boundary at precipitates, or a diffuse interface, which can “drag” an impurity cloud along analogous to impurity drag due to a Cottrell atmosphere of impurities around a dislocation [4,5]. Neither of these models is very accurate, since the diffuse interface description is not consistent with the fact that the actual grain boundary “thickness” is only a few atomic diameters, and the stress field surrounding the grain boundary has a very short range [6]. Atomic interactions and configurations are essential for accurate modeling. For this reason we have used molecular dynamics (MD) and Monte Carlo (MC) techniques in this study, since the atomic structure and local stresses are then fully represented.

We have measured grain boundary migration for systems with different concentrations of Fe. The initial distribution of the impurities is an important issue for this study, since the time scale feasible for MD simulations is relatively short, on the order of nanoseconds, and solid-state diffusion of Fe atoms is quite small. To approximate the conditions of real materials, which are likely to have achieved equilibrium levels of impurities and precipitates in the grain boundaries during fabrication, we start our simulations with a run based on the Metropolis MC algorithm. This method allows an initial distribution of impurities corresponding to equilibrium.

The nanocrystalline samples, were created using a Voronoi construction, with random location and orientation of the grains (see Fig. 1). It consists of 5 grains with a mean size of 5 nm and has dimensions of $40a_0 \times 40a_0 \times 40a_0$, where $a_0 = 3.62\text{Å}$ is the Cu lattice constant. Periodic boundary conditions are used in all three directions. The simulations are performed in an NVT ensemble after a short thermalization and volume relaxation under 0 pressure. Annealing of nanocrystalline samples was
performed for a range of temperatures and concentrations of Fe. After loading the samples with Fe and relaxing them at the chosen annealing temperature of 950 K, MD annealing runs of 100 picosecond were performed. A cross-section through a sample with 3% Fe is shown in Fig. 2. The majority of the Fe impurities (shown in red) is located in the GB, and small precipitates are formed.

![Figure 2. Configuration obtained after loading 3% Fe as described above.](image)

Figure 2. Configuration obtained after loading 3% Fe as described above.

Figure 3 shows cross sections of the Cu samples before and after the MD annealing. A single initial configuration, shown in Fig. 3(a), was loaded with different concentrations of Fe, and annealed. Color indicates orientation alone, and Fe atoms are not differentiated from Cu atoms. It is clear that during annealing GB's in pure Cu exhibits considerable migration, as shown by comparing Figs. 3, (a) and (b). The shrinkage of the central grain and the growth of its neighbors are clearly visible. Smaller GB displacements are observed when the system contains 0.6% Fe, as shown in Fig. 3(c). The sample with 3% Fe exhibits very small displacements for all grains. This result shows that impurities that segregate to the boundaries are able to stabilize the grain structure during annealing.

Our simulations show that small concentrations of low solubility impurities are capable of causing drastic reductions in GB mobilities. Our newly developed tools allow us to explore the important process of impurity segregation at GB and its effect on pinning, opening the possibility of modeling and designing extremely hard materials.

References

The Hall-Petch relation predicts that the hardness of polycrystalline materials increases with decreasing grain size, due to inhibited dislocation motion. But the possibility of taking full advantage of restricted dislocation motion in these materials seems to be limited to grain sizes above a critical size (10–30 nm); below this value, the strength decreases with decreasing grain size [1]. In this work we used molecular dynamics (MD) and Monte Carlo (MC) techniques to study the inhibition of grain boundary (GB) motion by impurity drag or precipitation mechanisms. The ability to pin the boundaries in this way may extend the region of normal Hall-Petch behavior to smaller grain sizes, and allow the fabrication of materials with greater hardness.

Experiments on nanocrystalline samples show that it is difficult to extract precise GB mobilities since they are derived from grains with various crystallographic parameters and a distribution of sizes that change continuously during annealing. For this reason, we used the U-shaped half-loop bicrystal shown in Fig. 1. This bicrystal was created by rotating grain 2 through 38.2° about the z-direction (a common ⟨111⟩ direction). This value of rotation corresponds to high symmetry Σ7 GB along the straight branches shown in Fig. 1 and provide the driving force for motion. In this geometry the driving force and the shape of the moving boundary segment remain constant during annealing. In addition, we have developed a new MD-MC simulation scheme that describes most accurately CuFe alloys thermodynamic properties and predicts correct Fe equilibrium concentrations in the GB and bulk [2].

Figure 2(a), shows a ⟨111⟩ projection of the final configuration after a 400 ps MD run of a Σ7 grain boundary (straight segments) plus the half loop in pure Cu at T=667 K. Only the higher potential energy atoms are shown to mark the location of the GB. After a short initial transient, a steady-state migration is observed. The driving force (GB energy per unit area) remains constant during the anneal. Figure 2(b) shows in turn the final configuration after a 400 ps anneal at T=1000 K of a sample loaded with 0.91% Fe using the MC-MD run. Although this concentration value is below the solubility limit for this potential, we can observe a weak segregation of Fe (depicted in red in the figure) at the GBs. It can also be observed that there is no impurity drag under these conditions, but depinning from the initial segregated Fe atoms occurs.

By monitoring the evolution of the half-loop during MD annealing we can obtain a measure of the effect of Fe impurities on grain boundary motion primarily
caused by pinning due to impurity segregation at GB's. Figure 3 shows a plot of the depinning time, \( \tau \), as a function of temperature, \( T \), for three different impurity concentrations: 0.0%, 0.34% and 0.91% Fe. We observe that as \( T \) decreases and Fe impurity concentration increases \( \tau \) increases and for some of the cases studied here is beyond 400 ps (the length of our simulations).

Figure 2. Snapshots of the final configurations of a \( \Sigma 7 \) half-loop GB for (a) pure Cu and (b) Cu with 0.91% Fe. Samples were annealed for 400 ps at a temperature of 667 and 1000 K for (a) and (b), respectively. The dashed line represents the initial position of the GB.

The inset to Fig. 3 shows an Arrhenius plot of the depinning time for the three samples studied. A substantial variation of the activation energy with impurity content is clearly observed: 0.05 eV for pure Cu and 0.15 eV for Cu-0.34% Fe. This result highlights the strong effect of impurities on mobility, even at low concentrations. GB depinning is the rate limiting process that controls GB mobility in a polycrystalline sample (GB motion in the solid solution does not play a significant role in determining the overall mobility). A GB moving through the polycrystalline sample will encounter impurity clusters left behind from segregation to other GB's.

Figure 3. Dependence of the depinning time, \( \tau \), on temperature for different impurity concentrations for the half-loop geometry shown in Fig. 1. The inset shows an Arrhenius plot of \( \tau \) for the same systems.

In summary, we have simulated curvature driven grain boundary motion using a hybrid Monte Carlo-molecular dynamics simulator. Our simulations show that Fe additions stabilize GB motion and that small concentrations of low solubility impurities are capable of causing drastic reductions in GB mobilities. The presence of 1% Fe caused an order of magnitude increase in the barrier for GB motion, and 3% Fe essentially immobilized GB's. Our newly developed tools allow us to explore the important process of impurity segregation at GB and its effect on pinning, opening the possibility of modeling and designing extremely hard materials.

References


Synthesis and Characterization of Nano-twinned, Ultrafine-Grained Copper


The production of new and improved high strength nanocrystalline (NC) and ultrafine-grained (UFG) materials is an endeavor that has been the subject of research for over two decades. Even though many advances have been made in processing techniques and improving the mechanical behavior of NC and UFG materials, the subject of large-scale production remains one of the biggest challenges in nanostructured materials research. In order for NC or UFG materials to be widely used, it is necessary to study feasible production methods with high reproducibility and scalability.

For a pure metal, such as copper, a variety of techniques have been employed to synthesize small grain structures, including electrodeposition, equal channel angular extrusion (ECAE), ball milling, and inert gas condensation [2-4]. One common issue of these processing techniques is that the sample dimensions are very small, typically in millimeter sizes. Moreover, these processes present a wide range of problems, such as impurity, porosity, texture, high surface roughness, and film thickness limitations [1-3], that lead to a large scatter in the mechanical behavior data. In many cases, such discrepancies can be attributed to the different processing techniques.

Historically, nanoscale multilayer technology is a process that uses a physical vapor deposition (PVD) technique to produce two-dimensional nanocomposites with fine alternating layer structures (<100 nm). Many types of nanoscale multilayers, such as Cu/Zr, Ni/Cu, and Ag/Cu alloys [4, 5], have been synthesized for applications such as protective coatings, mirrors, and sensors [3-12]. Currently, this type of technology has not been used to synthesize single element nanostructures (having nanoscale size features). This particular technique presents many advantages over conventional processing methods for nanoscale materials production: a) control of the bilayer thickness in order to tailor the mechanical properties, b) fabrication of large samples (diameter >10 cm), c) production of multiple samples during a single deposition run, and d) creation of samples with highly reproducible mechanical properties.

Here we present the large-scale production of UFG Cu foils with nanoscale twins processed by nanoscale multilayer technology (Figure 1). The synthesized foils are not considered multilayers since they are made of a single element. However, the techniques for processing the Cu foils arrived from multilayer technology, i.e., the foils were fabricated using five different layer thicknesses ranging from 1.25 to 43.6 nm (18,000 to 520 layers) for a total foil thickness of ~ 22 microns (Figure 2). We compare the effects of the deposition layer thickness to sample microstructure and mechanical behavior, all of which are unknown since this is the first time that multilayer technology has been adapted to process large-scale single element foils.

![Figure 1](image)

**Figure 1**: Copper foil process by multilayer technology: (a) attached to the substrate and (b) free-standing and placed perpendicular to foil (a). Note the smooth surface finish as both foil (a) and the coin reflect on foil (b).

Extensive TEM studies revealed very similar microstructures overall given a particular deposition layer thickness (Table 1). Despite the similarity in overall grain sizes, we emphasize the importance of the layer-by-layer deposition technique in reducing residual stress to allow large-scale production, in modifying the twin density, and in suppressing columnar grain growth. Smaller deposition layer thickness can be related to higher nanoscale twin density and, therefore, higher
strength. The tensile and indentation tests reveal a high strength Cu material that is attributed to the presence of nanoscale twins and ultrafine-grained structures. The Hall-Petch relationship for Cu as stated by Meyers and Chawla [13] for an average grain size of 200nm predicts a yield strength of ~270 MPa, which is much lower than our experimental values: 540 to 690 MPa (Figure 3).

Table 1. Characterization of UFG copper samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Number of layers</th>
<th>Deposition layer thickness (nm)</th>
<th>Twin-density (m²/m³)</th>
<th>Plan-view grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18000</td>
<td>1.2</td>
<td>3.0x10⁶</td>
<td>195</td>
</tr>
<tr>
<td>B</td>
<td>8350</td>
<td>2.7</td>
<td>not measured</td>
<td>179</td>
</tr>
<tr>
<td>C</td>
<td>4168</td>
<td>5.4</td>
<td>2.0x10⁶</td>
<td>177</td>
</tr>
<tr>
<td>D</td>
<td>2084</td>
<td>10.5</td>
<td>not measured</td>
<td>178</td>
</tr>
<tr>
<td>E</td>
<td>520</td>
<td>43.6</td>
<td>1.2x10⁶</td>
<td>175</td>
</tr>
</tbody>
</table>

We have demonstrated that nanoscale multilayer technology can be used for large scale production of fully dense, high purity (99.999%), nano-twinned, and ultrafine grained copper (14 samples per run, 10 cm diameter foils). Five different layer thicknesses were used ranging from 1.25 to 43.7 nm (18000 to 520 layers). Sample characterization revealed similar sample microstructures with medium twin densities. The yield strength for all five types of samples was in the range of 540 to 690 MPa, demonstrating that these materials are among the high strength coppers. Overall, the mechanical behavior of the UFG copper presented here compares favorably to other UFG samples processed by methods such as ECAE. Our process also has many advantages, such as large-scale production abilities, reproducibility, fully dense samples, a high-quality surface finish, and assurance of material purity.

Figure 2: TEM micrographs of copper foil produced by using 43.6nm deposition layer thickness a) plan-view noting a grain size of ~ 200 nm and b) cross-sectional view. Inset showing relatively high dense growth-twins inside columnar grains. Arrow denotes growth direction.

Figure 3: Summary of experimental data from literature for NC and UFG copper [14] including this study. The solid line indicates Hall-Petch relationship for Copper $\sigma_y (\text{MPa}) = 25.5 + 3478d^{-1/2}$ (nm) [13]

REFERENCES

In the search of mechanisms of grain boundary stabilization in nanophase materials, we have been performing molecular dynamics simulations of nanophase Cu with small amounts of Fe in solution.

In order to have realistic simulations of such system, we use a carefully tested potential that predicts a phase diagram quite in agreement with the real Fe-Cu system, whose principal characteristic is a very low solubility limit of Cu in Fe at room temperature. Figure 1 shows the solubility limit predicted by the potential we are using [1].

Besides the accuracy of the potential, a second important requirement for our research is to use a Metropolis Monte Carlo program with displacements able to deal with a large number of atoms. We have recently developed such a program, named MCCask and this work is one of its first applications.

In another contribution in this same report, we show the results of a simulation study of grain boundary stability as affected by Fe impurities, studied via the response of the nanocrystalline sample upon annealing. Our conclusion there is that small amounts of Fe are enough to significantly reduce the tendency of grains to grow. In this report we explore the influence of Fe to alter the mechanical response upon tension/compression.

Our nanocrystalline sample was built using the Voronoi polyhedra, with a density equal to 99% of the perfect crystal value, and including both high and low angle GBs in a random selection of grain orientations. Average grain size is 5 nm and sample size is ~ ½ millon atoms. Both pure and impure samples have the same grain structure to simplify the comparison of results. Figure 2 is a slice of the sample where Fe atoms are depicted in black.

It is apparent from this Figure the tendency of Fe to segregate at the grain boundaries when loading is performed at 800K. Stress strain curves at 300K for pure Cu and Cu-2% Fe are shown in Figure 3. It is apparent that Fe has a very small influence on plastic response.
Figures 4 show slices of both samples at 5% total deformation. Red atoms indicate locations of high displacement, i.e. the sources of plastic deformation.

![Stress-strain curves for pure nanocrystalline Cu and Cu-2% Fe under compression. Dotted line is the elastic response.](image)

**Figure 3:** Stress-strain curves for pure nanocrystalline Cu and Cu-2% Fe under compression. Dotted line is the elastic response.

It clearly appears, e.g. in the low-central part of the figures, how the presence of Fe alters the distribution of displacements: boundaries with Fe atoms hardly contribute to it.

This surprising result, i.e. Fe segregated at GB significantly alter the distribution of plastic deformation events but do not alter the overall plastic response of the sample nor its hardness, is somehow confirmed by experiments in which Fe is involuntarily incorporated into the sample as ball milling time increases without affecting yield strength [2]. Also confirmed by experiments is our yield stress of about 800 MPa.

A plot of the flow stress, defined as the saturation stress of the flat portion of the deformation curves in Figure 3, versus T gives the result shown if Figure 5. The slope is 1.8 MPa/K, in excellent agreement with the experimental value of 1.5 MPa/K.

![Flow stress versus temperature](image)

**Figure 5:** Flow stresses for pure Cu

References


We have been developing diamond technology and science to fabricate diamond ablators for inertial confinement fusion applications. We have proceeded by first coating plasma-enhanced chemical vapor deposited diamond on spherical silicon mandrels. We have manipulated the grain structure to produce micro-nanocrystalline grains to mitigate any anisotropy in the shock propagation in the diamond ablator. The coatings are then polished on the mandrel. A nanosecond pulsed laser is utilized to drill sub 20 micron diameter holes in the coating. Through the laser drilled holes the mandrel is etched out.
Inertial confinement fusion (ICF) target fabrication is one of the technical challenges that needs to be met for the successful operation of the National Ignition Facility (NIF). The baseline design for indirect-drive ignition targets for NIF consists of a two-millimeter-diameter spherical shell (“ablator”) with a wall thickness of 75-130 µm made of a low-Z material, filled with a frozen layer of deuterium-tritium (DT) fuel and a central DT gas core. Diamond seems to be a very promising material due to the following unique combination of physical properties: 1) the opacity/albedo properties of diamond for 250 – 300 eV photons, together with its high atomic density, provide efficient energy absorption and a high ablation rate that reduce Rayleigh-Taylor instabilities at the ablation front; 2) the extremely high yield strength of diamond allows for a room temperature handling of filled targets in which the DT fuel develops a pressure in the order of 1000 atm; 3) the broad-band optical transparency of diamond (from ultraviolet to far infrared, 0.22 – 20 µm) facilitates the use of optical techniques to smooth the DT ice layer thus assisting the intrinsic beta heating DT ice redistribution; and 4) finally, the high thermal conductivity (up to 23 W cm⁻¹ K⁻¹ at 300 K) of diamond simplifies the cryogenic system requirements.

We recently developed a process to fabricate high-quality diamond shells with a surface finish on the nm length scale (Figure 1). The process involves the following steps: 1) chemical vapor deposition of diamond on silicon mandrels, 2) polishing of the initially rough diamond films to the required surface finish, 3) microfabrication of blind holes through the diamond film or, alternatively, microfabrication of through-holes (through the silicon mandrel, 4) removing of the silicon mandrel by an etch process, and 5) attaching a fill tube or plugging the fill hole.

Deposition of optical-quality diamond films on spherical silicon substrates with a diameter of 2 mm was performed at the Fraunhofer Institute, Germany using a 6 kW microwave reactor optimized for long-term plasma stability. The system is equipped with a custom-designed substrate holder to guarantee the homogeneous coating of spherical substrates (Fig. 2a). The diamond films were grown at 700-900 °C using a feed gas mixture of 1% methane in hydrogen resulting in a deposition rate of ~ 2 µm/h. Figure 2b shows a set of spheres simultaneously coated with an ~70-µm-thick diamond film.

The as-grown diamond films exhibit a very rough surface morphology due to the coarse grain structure of CVD diamond. We adopted polishing techniques used in the ball bearing
industry to fabricate brittle ceramic balls. A typical setup consists of a rotating grinding disk (charged with diamond powder) and a sample holder with concentric grooves which is used to press the diamond coated spheres against the grinding disk. First experimental results look already very promising.

In order to remove the Si mandrel, micron-sized holes have to be drilled through the diamond film. The same holes can later be used for filling the target with DT. The specifications for NIF baseline capsules requires fill holes with a diameter of <5 µm. Using laser based micromachining we are able to drill round, tapered holes with diameters as small as 5 µm through ~100-µm-thick diamond films. Using the holes prepared as described above, the Si mandrel can than be removed by wet etch techniques (Figure 3).

Finally, the hole can be plugged with diamond-like carbon (DLC) using a focused-ion-beam assisted chemical vapor deposition process (Fig. 4).

Figure 2. Deposition of optical-quality diamond films on spherical silicon substrates: (a) Custom-designed sample holder consisting of a rotating beveled inner disk and a stationary outer ring, with the Si mandrels inserted into the groove between the inner disk and the outer ring. (b) Set of Si spheres simultaneously coated with an ~70-µm-thick diamond film.

Figure 3: Hollow diamond shells fabricated by the process outlined above.

Figure 4. FIB-assisted microfabrication technique: plugging of a hole drilled through a free-standing Cu foil by FIB-assisted chemical vapor deposition (FIB-CVD).
Diamond, the hardest known material, presents many unique polishing challenges. Here we demonstrate how advanced surface analysis techniques improve the understanding of polishing mechanisms for polycrystalline diamond surfaces at the nanometer scale.

For many applications, it is important that the polycrystalline diamond surface be made as smooth as possible. For example, for diamond lenses or optical windows, a rough surface scatters light and creates optical losses. Diamond is also an excellent thermal conductor, and is therefore useful as a highly efficient heat sink. However, the conduction of heat into diamond can be limited if the diamond surface is too rough, since topography limits the effective diamond contact area with the material that is to be cooled. For the National Ignition Facility (NIF) spherical ablator, the surface roughness is a critical parameter. Variations in surface height are equivalent to variations in the ablator thickness, and small changes in this thickness may cause instabilities during ignition.

The only efficient method for polishing a diamond is with another diamond. This is generally accomplished by bringing the diamond surface to be polished into contact with a rapidly rotating metal surface that has been charged with diamond particles, often in the presence of lubricating liquid such as oil. Smoothing polycrystalline diamond is made more difficult by the fact that the polishing rate depends strongly on the crystallographic orientation of the surface being polished, as well as the direction of polishing.

A polycrystalline diamond surface has a wide range of orientations present, as shown in Fig. 1. Colors indicate the crystallographic orientation parallel to the surface normal.

Fig. 1 was obtained with a scanning electron microscope (SEM) technique that makes use of electron backscattered diffraction (EBSD) patterns generated locally by the interaction of the electron beam with the surface. While the technique is typically used to map planar surfaces, as shown in Fig. 1, we have also mapped regions of a spherical surface (Fig. 2).

Relative grain heights and surface topography are measured with atomic force microscopy (AFM). The crystallographic anisotropy of the diamond polishing rate makes it straightforward to develop one-to-one correlations between AFM topographies and EBSD crystallographic maps, as shown in Fig. 3. Here it is apparent that domains of similar height have the same crystallographic orientation.

Diamond grains which have a [111] crystallographic direction parallel to the surface normal have the highest in-plane atomic density, and in general, polish slowest. Therefore, the {111} grains are the highest grains on the polished polycrystalline diamond surface. These can then be used as references for determining the relative heights of other nearby grains. By measuring the {111}-referenced heights of many diamond grains, and plotting them on a single
stereographic triangle (Fig. 4), a pattern emerges which can be understood with atomic-scale models of bond density and directionality.

Fig. 3  Orientation map of polished diamond surface (a), with AFM image (b) of the same surface.

Fig. 4  Relative diamond grain depth as a function of crystallographic orientation

Polishing rate does not depend solely on in-plane atomic density, as can be seen in Fig. 4: [111]- and [001]-oriented grains have significantly different densities, yet polish similarly. A key concept for understanding diamond polishing is the periodic bond chain (PBC). The PBC is defined for any crystal lattice as "an uninterrupted chain of bonded growth units connecting two translation-equivalent lattice positions." The single most important variable for determining polishing rate is the orientation of the polishing direction relative to the nearest PBC vector.

The PBC model is useful even though in-plane polishing direction is typically varied randomly throughout the polycrystalline diamond polishing process. There are six crystallographically-equivalent PBC vectors in diamond. For a given grain orientation, we determine the number of PBC vectors within a few degrees of the surface plane, and find an excellent correlation with polishing efficiency, as shown in Fig. 5.

Fig. 5. Average grain depth vs. the number of diamond PBC vectors within 10 degrees of the surface plane

We can now apply this information to synthesize a diamond surface that will have a crystallographic texture that polishes much more uniformly. EBSD and AFM analysis can be performed on spherical surfaces, so the approach is well-suited for development of ultra-smooth polycrystalline diamond ablators for NIF.

Developing processing techniques for targets: hole drilling and mandrel etching

Juergen Biener, Alex V. Hamza (LLNL), Christoph Wild, Eckhard Woerner, and Peter Koidl (Fraunhofer Institute for Applied Solid-State Physics)

Developing a toolbox of state-of-the-art processing techniques for NIF (National Ignition Facility) target fabrication is necessary to meet the stringent specifications required for inertial confinement fusion (ICF) experiments. Among the most important techniques required are 1.) fabrication of micron-sized holes through NIF capsule ablator materials, and 2.) removing the mandrel material via an etch process. Here, we report on our recent progress in developing these processing techniques for diamond NIF capsules.

We developed the capability to drill micron-sized holes through approximately 70 micron thick diamond films using a diode pumped, q-switched Nd:YAG laser with a repetition rate of 4 kHz and an average laser power of 10 W. Figure 4 shows an example of such a hole. Note that the exit hole diameter is only 5 micron.

These holes can then be used to remove the mandrel material (silicon) which was needed to grow a spherical shell of ablator material (diamond). The challenge is find a process which allows us to remove the mandrel material through the required small holes (≤ 5 micron diameter) within a few days. To achieve this goal we are currently testing both wet and dry etch techniques.

Figure 2 shows a hollow diamond shell which was obtained by a wet etch technique. In this example, the silicon mandrel was removed through a ~20-micron-diameter hole.

In parallel we are establishing the capability to use fluorine-based dry etch techniques. We developed a setup which allows us to run computer-controlled etch cycles (Fig. 3).

Figure 1: Laser-drilling through diamond: Entrance (a) and exit (b) hole machined though an approximately 70-micron-thick diamond film.

Figure 2: Hollow diamond shell cut into two pieces to demonstrate the complete removal of the silicon mandrel.

Figure 3: Experimental dry etch setup including computer-controlled gas valves (v) and a pressure sensor (p).
Diamond films are very attractive for many applications such as anti-wear coatings, optical windows, and electrochemical electrodes, where mechanical strength and hardness, optical transparency, and chemical stability are required. A wide range of diamond microstructures has been reported in the literature for the past several decades [1]. For example, microcrystalline diamond films, grown by chemical vapor deposition (CVD), can be made hundreds of microns thick and are, therefore, valuable as robust mechanical-wear layers or as freestanding optical windows. Nanocrystalline diamond (NCD) and related so-called “ultrananocrystalline” diamond (UNCD), by contrast, have other functional advantages: these are smoother than microcrystalline diamond films and can be made electrically conductive [1]. Both NCD and UNCD, however, have previously been demonstrated only in films that are at most a few microns thick. Growth of thicker films is often hindered by the development of high stresses during film deposition [1].

We have applied a hot-filament CVD process for growing freestanding nanostructured diamond films, ~80 µm thick, with residual tensile stress levels ≤90 MPa. We have characterized the film microstructure, mechanical properties, chemical bond distribution, and elemental composition. Results have shown that our films are nanostructured with columnar grain diameters of ≤150 nm and a highly variable grain length along the growth direction of ~50-1500 nm. These films have a rms surface roughness of ≤200 nm for a 300× 400 µm² scan, which is about one order of magnitude lower than the roughness of typical microcrystalline diamond films of comparable thickness. With our deposition method, the grain size does not increase with increasing film thickness, which we attribute to a high rate of secondary nucleation, as evidenced by a high density of planar defects within the grains. Ultrathick films can be grown because internal stresses in these films are much lower than the stresses which have previously been observed for NCD and UNCD films [2, 3].

Figure 1: Bright-field (a) and dark-field (b) XTEM images of the nanostructured diamond film, showing an area of the cross-section with a large, elongated crystallite and a number of smaller crystallites. Both images are of the same magnification. The inset in (b) shows a higher magnification bright-field image illustrating a large density of planar defects within the grains.

The microstructure of our NCD film is illustrated in cross-sectional transmission electron microscopy (XTEM) images in
Fig. 1, showing an area with the largest crystallite that we have observed examining three TEM cross sections extracted from different parts of the NCD film. A comparison of bright-field [Fig. 1(a)] and dark-field [Fig. 1(b)] images taken from the same area of the cross section illustrates the nanostructured character of the film.

To estimate the relative $sp^2/sp^3$ bond fraction, NCD films were studied by x-ray absorption near-edge structure (XANES) spectroscopy. Figure 2 gives a comparison of C $K$-edge XANES spectra of graphite, the NCD film, and a diamond single crystal. A comparison of spectra for the NCD film and a diamond single crystal in Fig. 2 provides evidence of the good quality of our NCD films. The small, broader peak at $\sim$285.4 eV in Fig. 2 in the NCD spectrum is assigned to the $1s \rightarrow \pi^*$ transition of $\pi$-bonded carbon (i.e., $sp^2$ carbon) [4]. The low intensity of this $sp^2$-related $\pi^*$ peak in the spectrum of NCD (compared to its intensity in the spectrum from graphite also shown in Fig. 2) clearly demonstrates that $sp^2$-type bonding is dominant in our NCD films. The relative fraction of $sp^2$ bonds of $\sim$10% in NCD films can be roughly estimated by taking the ratio of the maximum intensities of the $\pi^*$ peak at $\sim$285 eV and the broad $\sigma^*$ resonance at $\sim$291 eV. This result is not unexpected since C atoms at grain boundaries in NCD and UNCD are typically $sp^2$ hybridized [1]. The large percentage of $sp^3$ bonding in the films revealed by XANES is consistent with a high hardness of 66 GPa measured by nanoindentation. Nanoindentation and XANES results are also consistent with a high phase and elemental purity of the films, directly measured by x-ray and electron diffraction, Rutherford backscattering spectrometry, and elastic recoil detection analysis.

**References**


The synthesis and characterization of nanoporous materials has been a major theme for the NSCL. We have been pursuing three techniques to fabricate ultra-low density nanoporous metals: atomic layer deposition on aerogels, growth on and assembly of templates, and dealloying. The first two techniques are “bottoms up” approaches that build on our expertise on the synthesis of oxide aerogels. The third technique is a “top down” approach that relies on self-assembly during material removal. To our surprise these nanoporous materials have been stronger than would be predicted by macroscopic scaling laws. This is another example of the length scale (in the nanometer regime) producing novel properties.
Template-Directed Fabrication of Nanoporous Metal Foams using Atomic Layer Deposition

The design of nanoporous metals is currently an active area of research since materials of this type hold technological promise for a wide range of applications including catalysis, energy storage and conversion, sensors/detectors and nanoelectronics. Traditional methods for the fabrication of nanoporous metals involve either a “bottom-up” approach, such as aggregation of metal nanoparticles, or “top-down” techniques, such as dealloying. These methods, however, offer limited control over morphology of the resultant structure. A powerful method for controlling pore sizes and densities in cellular materials is the template approach. This technique involves three basic steps: (1) fabrication of a template with desired structural features, (2) infusion of the target material into the voids/pores of the template and (3) removal of the template to yield the replicate solid. Depending on the type of template used, cellular materials with pore sizes ranging from microns down to a few Angstroms can be prepared. Aerogels are a special class of open-cell foams with sub-micron architectures, and, as such, are ideal templates for the preparation of nanocellular metal foams. For infusion into these templates, we are using atomic layer deposition (ALD) since the process provides both atomic layer control of thin film growth through sequential, self-limiting surface reactions as well as excellent film conformality on high aspect ratio structures. We are applying this template-directed ALD approach to the preparation of low density porous metal foams with sub-micron pore sizes and, in the next three sections, we describe our progress with three different metals.

Fig. 1 TEM images of (a) AlOOH and (b) GeO₂ aerogel monolith

A. Tungsten Foams
For the tungsten foams, we used two different types of aerogel templates: (1) low-density alumina aerogels (70 mg/cc) with nanoribbon ligaments (Fig. 1a) and (2) low-density germania aerogels (35 mg/cc) with elongated nanorod ligament morphology (Fig. 1b). The deposition of tungsten films on these templates was performed through alternating exposures of disilane (Si₂H₆) and tungsten hexafluoride (WF₆) at 300°C. Substantial weight gains (up to 2000%) were measured for both type of template after several cycles. The morphologies of the coated aerogels were examined by
transmission electron microscopy (TEM) and are shown in Fig. 2. The excellent uniformity and conformality of the coatings are clearly demonstrated for both systems. Examination of the W-coatings by x-ray photoelectron spectroscopy (XPS) showed that the deposited tungsten completely oxidized upon exposure to air. In the case of thicker coatings, the resulting WO₃ layers protect the underlying metallic W layers from further oxidation. These oxidation layers can be removed through treatment with a hydrogen plasma and are not expected to have adverse effects on the production of high-quality nanoporous metal structures.

Fig. 2 TEM images of (a) AlOOH aerogel and (b) GeO₂ aerogel monoliths coated with tungsten after 6 cycles, showing excellent uniformity and conformality of the coating.

B. Ruthenium Foams

Since ruthenium is a noble metal, complications arising from the oxidation of the resulting nanoporous metal structure are minimized. Atomic layer deposition of ruthenium metal involves the treatment of a substrate with bis(cyclopentadienyl)ruthenium (RuCp₂) followed by decomposition of the organic Cp ligands with oxygen. This approach was used to deposit Ru metal on carbon aerogel templates. Microstructural analysis shows that the carbon aerogel network is uniformly coated with metallic Ru nanoparticles, 5-20 nm in size (Fig. 3). The metallic character of the deposited Ru was confirmed by XPS and time-of-flight secondary ion mass spectroscopy (TOF-SIMS).

C. Copper Foams

Copper ALD entails the deposition of organometallic Cu complexes on a substrate, followed by reduction with an organic reagent, such as formaldehyde or ethanol. Our work in this area started with CuO ALD, a model system that will allow us to determine the optimal reaction parameters (i.e. precursor, temperature, cycle times) for uniform deposition of copper metal on aerogel substrates. We treated an ultra low-density SiO₂ aerogel (10 mg/cc) with alternating cycles of copper(II)-acetylacetonate (Cu(acac)₂) and ozone, affording a CuO-coated silica aerogel. Characterization of the material showed that, while CuO was indeed deposited in the pores of the aerogel (Figs. 4 and 5), the concentration of Cu decreases with increasing distance from the outer surface of the aerogel monolith. This gradient in CuO deposition is due to incomplete diffusion of the precursor into the pores of the template and limited reactivity of Cu(acac)₂ with the substrate surface. To address these issues, we are examining other Cu precursors that exhibit the requisite volatility, thermal stability and reactivity for uniform
deposition. For example, we have initiated work with Cu(I) N,N’-di-sec-butylacetamidinate that has recently been shown to deposit conformal Cu and CuO films on silica substrates.

![Image](image1)

**Figure 3:** Aerogels can be uniformly coated by ALD. (a) Low-magnification SEM micrograph of a Ru coated carbon aerogel. (b) Detail of a fractured carbon ligament revealing a conformal Ru coating. (c) HRTEM micrograph demonstrating the nanocrystalline character of the Ru coating.

![Image](image2)

**Figure 4.** SEM image of a silica aerogel coated with CuO (scale bar is 100 nm).

**Future Work**

Our initial studies with these metals have shown that the ability to deposit uniform metal films is intimately tied to the surface chemistry and porosity of the aerogel template. Therefore, a critical element of this effort is the ability to tailor the synthesis of the organic and inorganic aerogels such that these templates possess the requisite surface properties for optimal precursor adsorption and conversion.

As these techniques evolve and new materials are prepared by ALD, emphasis will be placed on removal of the aerogel template. Carbon-based templates can likely be removed thermally, while inorganic templates (such as silica or germania) will be chemically dissolved or etched from the replicate metal foam.

![Image](image3)

**Figure 5.** Elemental mapping (x450) of Cu and Si in the CuO-coated silica aerogel.

**References**


Aerogel Templating of Gold Foams
Gregory Nyce, Ted Baumann, Joe Satcher

Organic templating is a technique used to prepare low-density metal sponges. The organic template directs the formation of the metal framework and then is removed to leave a porous metal sponge. Organic aerogels are attractive templates for porous metal foams due to their high surface areas (400 – 1000 m² g⁻¹) and small pore size (≤ 50 nm).¹

We have developed a new method using gold nanoparticles as sol precursors to prepare gold/thiophenol aerogels. Organic aerogels are synthesized through a sol-gel process that occurs in two stages. In the first stage, organic precursors are polymerized to form an aqueous colloidal sol. Once the sol is formed in-situ, the sol particles crosslink to form a three-dimensional gel network. Our approach is to use gold nanoparticles as sol precursors for aerogel synthesis, Scheme 1. The gold nanoparticles (≈ 10 nm) were synthesized with a thiophenol passivating layer on the surface of the particles that prevents agglomeration of the particles and allows the particles to be easily dispersed in water to form the initial sol solution.² In addition, the thiophenol layer allows the particles to be crosslinked into a gel when placed in an alkaline solution of formaldehyde. Supercritical extraction of the wet gel exchanges the liquid with air while effecting minimal perturbation of the template structure. A dry monolith (ρ ≈ 300 mg/cc) is shown in Figure 1. The BET/BJH analysis of the monolith is consistent for an aerogel having high surface area (365 m²/g) and small average pore size (18 nm).

Removing the organic template from the aerogel monolith has been difficult. By TGA analysis, we estimate the organic template is 55% weight percent of the total monolith weight. Initial attempts to remove the organic material by heating in air have been unsuccessful due to significant densification and coarsening of the gold framework. As an alternative to heat treatment, we have used a chemical etching solution of HNO₃/H₂SO₄ (50:50 v/v) that selectively etches away the organic template from the gold foam framework. The chemically etched gold foam structure (ρ ≈ 1 g/cc) has <5 µm voids and ligament sizes of 200 nm, smaller features than dextran templated gold foams, Figure 2. This gold foam can be further machined into a halffraum part, Figure 2. Unfortunately, the chemical etching
protocol has not been reproduced and thus it’s utility may be limited.

Figure 1. Image of gold/thiophenol aerogel.

Figure 2. A. SEM image of HNO$_3$/H$_2$SO$_4$ etched gold foam. B. Machined halfraum of HNO$_3$/H$_2$SO$_4$ etched gold foam.

We have also examined the utility of oxygen plasma as an organic etchant. Oxygen plasma is a mild way of etching away the organic template however we have only succeeded in etching away approximately 30 - 50 µm from the surface, far short of the minimum requirement of 300 µm, Figure 3. The structure of the gold foam prepared by oxygen plasma treated has dense regions of gold while other regions have 20 µm voids. The overall inhomogeneity of this gold structure may make it incompatible for laser target applications.

Figure 3. A. Image of 30 µm gold foam etched by oxygen plasma. B. Fracture surface of gold aerogel showing growth of gold ligaments where the organic has been etched away.

Using gold nanoparticle building blocks, we have prepared aerogel monoliths. The monoliths are 45% gold by weight and the gold is homogenously dispersed throughout the monolith. We have had limited success in removing the organic template from the aerogel using chemical and oxygen plasma etching techniques. Chemical etching of the organic template did produce a gold sponge with finer features than gold sponges prepared with dextran templates. Other etching techniques, such as UV/Ozone etching, will be investigated in future work.

References

Organic Templating of Gold and Platinum Metal Sponges
Gregory Nyce, Ted Baumann, Joe Satcher

Organic templating is a technique used to prepare low-density metal sponges. The organic template acts as a scaffold to direct the formation of the metal sponge. Once the metal sponge is formed, the template is removed leaving a free-standing metal sponge. Dextran is an organic template that has been used to template porous gold and silver sponges. The dextran template is dissolved in water with a metal precursor and then removed by heating in air at 500-600 °C leaving a porous metal framework. Dextran templating is simple, versatile, and amenable to scale-up, however, to reproducibly achieve monolithic gold and platinum sponges with voids less than 10 µm and densities less than 1 g/cc is difficult.

We have introduced two modifications to the dextran templating procedure that improve structure and reproducibility of prepared gold and platinum sponges. First, gold and platinum nanoparticle building blocks were synthesized, Figure 1. The gold particles (500 nm) and platinum particles (50 – 100 nm) were suspended in a dextran/water solution and then freeze dried. Freeze drying removes the water from the solution to yield a dried dextran/metal monolith.

Heating the monolith to 500 °C removes the dextran template while sintering the metal particles to form a monolithic metal sponge, Scheme 1. Prepared gold and platinum foams are shown in Figure 2. Densities of the gold and platinum sponges are approximately 1 g/cc.

Scheme 1: Preparation of gold sponges using gold particles and dextran.
The sponges are comprised of a 3-D network of sintered gold and platinum particles as observed in the SEM images, Figure 3. There appears to be little size difference between the as synthesized gold and platinum particles and the particles in the sponge suggesting minimal growth of the metal particles during the sintering process. The structures are fairly uniform with voids of 1 - 10 µm. Coarsening of the gold structure occurs at 500 °C with gold particles < 500 nm to form large ligaments while coarsening of the platinum particles is observed at 800 °C. Differing coarsening temperatures between gold and platinum is likely a result of the increased surface diffusivity of gold relative to platinum.3

We have demonstrated the use of dextran templates to synthesize metal foams. These foams can then be machined into halfraum pieces for laser target applications. Future work will focus on organic templating optimization and other synthetic avenues toward metal foams.

References
Mechanical Behavior of Nanoporous Metal Foams – Scaling Factors
A.M. Hodge, J. Biener, J.R. Hayes, Y.M. Wang, P.M. Bythrow, A.V. Hamza

Metallic foams with pore sizes from 250µm to 2mm have been a subject of research due to their high surface area, which allows for a variety of applications, such as heat transfer and sound insulation [1-3]. Recently, processing of metallic foams at the nanoscale (pore sizes less than 100 nm) has opened the door to new and interesting applications, such as sensors and actuators [4, 5]. In general, processing of nanoporous metal foams has been focused on selective dealloying techniques with some exceptions [4]. Figure 1 depicts a typical structure for a nanoporous metal foam processed by dealloying.

Currently, research of nanoporous metals has been focused on synthesis. However, in order to further study possible nanoporous foam applications, their mechanical behavior needs to be addressed. It is known that nano-structured bulk materials exhibit novel mechanical properties [6-8]. Therefore, it is expected that nanoporous materials would also behave differently from macro-cellular foams, thus presenting a new field of study. Few studies have been focused on macro-foam behavior, such as Li et al. who reported a ductile-brittle transition in nanoporous Au, which seemed to be controlled by the microstructural length scale of the material [9]. Biener et al. reported on the fracture behavior of nanoporous Au as a function of the length scale [10]. Recently, we studied the mechanical properties of nanoporous-Au under compressive stress by depth-sensing nanoindentation, and determined a yield strength of 145 (±11) MPa and a Young’s modulus of 11.1 (± 0.9) GPa [11]. A striking result of this study is that the experimentally determined value of the yield strength is almost one order of magnitude higher than the value predicted by scaling equations developed for open-cell foams [2], thus potentially opening the door to the development of a new class of high yield strength / low density materials.

We have recently presented an overview of issues which can affect the mechanical behavior of nanoporous metallic foams such as ligament size, grain size, fracture mechanisms and testing parameters [12]. Here we present the effects of relative density and how it affects the current scaling equations at the nanoscale.

By using dealloying techniques and modifying the processing conditions, we can achieve ligament sizes ranging from 5 to 900 nm (for Au and Cu foams), which allows the study of a wide range of parameters including the relative density.

![Figure 1 SEM micrographs of dealloyed 25% Au foam by a) free corrosion and b) electro-chemically driven (EC).](image)

From Gibson and Ashby we can use the following equations to understand the foam behavior as a function of the relative density (density of the foam/density of the bulk):

\[ E^* = C_1 E_s \left( \frac{\rho^*}{\rho_s} \right)^2 \]  
Eqn. 1

\[ \sigma^* = C_2 \sigma_s \left( \frac{\rho^*}{\rho_s} \right)^{3/2} \]  
Eqn. 2

where * refers to foam properties and s to the bulk properties, and \( C_1=1 \) and \( C_2=0.3 \) are constants. Equations 1 and 2 are plotted in Figure 2 to demonstrate that the nanoporous foams do not
follow the Gibson/Ashby scaling equations for macro-porous foams. From figure 2b, the strength vs. relative density shows the same slope for nanoporous materials when compared to Gibson/Ashby; however, the nanoporous foams have a strength that is a factor of ~15 higher than predicted. The elastic modulus presents a large difference compared to the scaling equations. This discrepancy can be due to a deformation mechanism different from the cell edge bending model proposed by Gibson and Ashby. Another factor which is not currently accounted for is the nanoscale size of the ligaments, which present a Hall-Petch like effect. Studies on the ligament size are currently underway, and it is expected that ligament size will strongly affect the mechanical behavior.

Many advances have been made in understanding nanoporous materials, specifically nanoporous gold. New issues arise regarding the mechanical behavior of nanoporous foams compared to macro-cellular foams. These issues are somewhat analogous to comparisons between metals with nanocrystalline grain sizes vs. micron-millimeter size grains and their effect on mechanical behavior.

We have also shown that a) the yield strength and elastic modulus of nanoporous foams do not follow the Gibson/Ashby scaling equations, and that b) nanoporous foams are a high yield strength material. Overall, this article presents the potential in developing nanoporous foams as a new class of high yield strength / low density materials.

REFERENCES


![Figure 2. Plots using Gibson and Ashby scaling equations vs. relative density for a) normalized elastic modulus and b) normalized yield strength. The nanoporous Pt sample was provided by Dr. J. Weissmueller [4].](image-url)
Low Density Nanoporous Metals by Dealloying Ternary Alloys
J.R. Hayes, J. Biener, A.V. Hamza, K. Sieradzki (Arizona State University)

Dealloying creates an ideal nanoporous metal with a bicontinuous ligament structure (see section entitled “Monolithic Nanoporous Cu by Dealloying” for a general introduction to dealloying theory). However, when dealloying a binary alloy, 25% relative density is the lowest limit that can be achieved for most systems before structural collapse occurs. In order to access the lower densities needed for inertial confinement fusion targets, novel processing techniques must be employed. Once such technique is to dealloy a ternary alloy.

The alloy composition would be \( A_{1-x-y}B_yC_x \) with the constraints \( x/y \geq 0.25 \) and \( (x+y)/(1+x+y) \geq 0.25 \).

The ternary system Cu-Ag-Au satisfies requirements 2 and 3. By special processing, such as melt spinning, a near solid solution alloy can be formed. However, x-ray diffraction indicates that some phase segregation into a copper rich and a silver rich phase is occurring. This alloy was dealloyed by placing it direction in 70% HNO\(_3\). The kinetics of copper dissolution is much faster than that of silver dissolution in this environment. As a result of this, and of the phase separation, the alloy was able to restructure during dealloying to yield a pure gold porous structure with a relative density below 25%. While fragile, a stable structure was created. Figures 1 and 2 show the results of this method.

In order to dealloy a ternary system, three conditions must be met:
1) The alloy must be formed into a solid solution or a homogenously mixed structure, either through heat treating or mechanical processing.
2) The redox potentials of the three components must be sufficiently separated to allow selective individual oxidation of one component at a time.
3) None of the components can be subject to passive film formation.

Figure 1: The structure resulting from dealloying Cu\(_{70}\)Ag\(_{20}\)Au\(_{10}\) in a single step in 70% HNO\(_3\). A pure gold structure results with ligaments \(~40\text{nm}\) in diameter. The overall density of the structure is 10%.

In order to create a more uniform and robust structure, the dealloying can be carried out in two steps. First, the copper is removed, and then the resulting porous
structure is coarsened by Ostwald ripening through an annealing step. The resulting Ag/Au porous structure is then further dealloyed to create a bimodal pore distribution. The large coarsened ligaments will provide structural stability, with the secondary dealloyed pores lowering the overall density.

This two stage dealloying can be done electrochemically by driving a sample at different potentials. A Cu70Ag20Au10 sample was dealloyed electrochemically by driving it at 500 mV vs. Ag/AgCl. The resulting structure is seen in Figure 3. An extremely small pore size of ~10 nm resulted. This structure can then be annealed and the silver removed.

A sample created by simply melting the appropriate amounts of Cu, Ag, and Au was formed for a two stage dealloying process. The Cu was removed, and then the structure was coarsened by annealing. The sample was then placed in concentrated nitric acid to remove the silver. This created the bimodal pore structure seen in Figure 4.

By using the ternary dealloying strategy, densities as low as 6% have been achieved. In order to push this density even lower, this technique will need to be combined with other techniques to create a starting ternary alloy of less than 100% density. For instance, dextran templating using Cu/Ag/Au can be used to create a starting material of <30% density, which can then be dealloyed. This may also aid in the machining and handling of the samples, which can be done before dealloying while the materials is more robust. Dealloying does not change the overall dimensions of the sample so it can be done as a final step to achieve the density required for the target.

Figure 3: The structure resulting from dealloying Cu70Ag20Au10 by driving it potentiostatically at 500 mV vs. Ag/AgCl. A porous Ag/Au alloy was formed, with ligaments ~10nm in diameter.

Figure 4: The bimodal pore structure resulting from a two step dealloying process, with an intermediate anneal to coarsen the structure. The starting alloy was Cu70Ag20Au10.
Morphological control of nanoporous gold by surfactants

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Nanoporous Au (np-Au) prepared by dealloying of Ag-Au alloys has attracted considerable interest due to potential sensor, catalyst, and actuator applications. The surface is expected to play an important role in determining the stability of this material as the open sponge-like morphology results in a very high surface-to-volume ratio. In order to study the influence of surface chemistry on pattern formation during dealloying as well as on the stability of the resulting structure against coarsening, we employed ion-bombardment of Au(111) surfaces as a model system: Both dealloying and ion-bombardment generate a supersaturation of Au adatoms and vacancies, which in turn results in the nucleation of Au adatom clusters and vacancy islands. This similarity explains the similar appearance of dealloyed Ag-Au samples and ion sputtered Au(111) surfaces (Fig. 1).

Figure 1: Comparison of a SEM micrograph from np Au with a STM image collected from an Ar$^+$ ion-bombarded Au(111) surface.

This resemblance suggests that ion bombardment experiments can be used to study the influence of oxygen adsorption on pattern formation during dealloying. Indeed we observe that the presence of adsorbed oxygen (as little as 0.3 monolayer) decreases the feature size of ion-bombarded Au(111) surfaces (Figure 2): Both Ar$^+$ and O$_2^+$ ion-bombarded Au(111) surfaces exhibit the same pit-and-mount surface morphology, but the characteristic length scale observed after oxygen-ion bombardment is approximately five times smaller. Furthermore, annealing experiments reveal that adsorbed oxygen stabilizes the ion bombardment induced surface roughness against thermally-induced coarsening. These observations can be explained by a stabilizing effect of oxygen on undercoordinated Au atoms. This finding has long-reaching implications for the potential application of gold-based catalysts which is currently hampered by the limited thermal stability of nano-dispersed Au particles.

Figure 2: STM images (200 nm x 200 nm) showing the steady-state morphology of O$_2^+$ (top panel) and Ar$^+$ (bottom panel) ion bombarded (~ 6 x 10$^{15}$ ions/cm$^2$) Au(111) surfaces before and after annealing at the indicated temperature. Oxygen ion bombardment leads to a higher nucleation density of both adatoms and vacancies, and increases the thermal stability of the rough surface morphology.
Low density, homogeneous nanoporous metals are critical for current NIF hohlraum and double shell target designs. Such a structure can be achieved through the electrochemical process of dealloying, whereby one component of an alloy is removed and the remaining component restructures into a bicontinuous open pore structure(1,2). Dealloying occurs when an alloy $A_pB_{1-p}$ is immersed in an electrolyte with a driving force such that the more reactive component $A$ is oxidized and solves into solution, and the more noble component $B$ remains stable in metallic form. The driving force can be an applied potential or a suitable oxidizing solution. The elements remaining after dealloying often form a nanoporous structure.

While any alloy that meets the electrochemical criteria may be dealloyed, ideal bicontinuous porous structures are obtained from binary alloys with complete single phase solid solubility across all compositions. The Cu alloy that best fits both the metallurgical and electrochemical requirements is Mn/Cu. The phase diagram indicates that a solid solution alloy could be made through a precise heat treatment. The standard reversible potential of Mn is -1.135 V SHE, whereas Cu is 0.342 V SHE. The 1.477 V difference makes this alloy an ideal candidate for dealloying.

Mn/Cu can be dealloyed by free corrosion in several different electrolytes, and by driving potentiostatically. Completely dealloyed samples had a relative density ($\rho_{\text{sample}}/\rho_{\text{Cu}}$) of 30 ± 2%, as determined by the mass and volume of the dealloyed sample.

Dealloying in different electrolytes leads to significantly different ligament morphologies and length scales, yet all of the electrolytes still generate a bicontinuous ligament structure. Fig. 1a-d shows FESEM images of the samples dealloyed in 4 different electrolytes: (a) pH 1.3 HCl, (b) 1 M citric acid, (c) 0.01 M H$_2$SO$_4$ + 0.001 M MnSO$_4$, and (d) 1 M (NH$_4$)$_2$SO$_4$ + 0.01 M MnSO$_4$.

The large difference in ligament size and structure is dependent on the dealloying rate and the surface mobility of Cu in the given electrolyte. The effect of dealloying rate is especially apparent in Fig. 2. A Mn$_{0.7}$Cu$_{0.3}$ sample was dealloyed by free corrosion in 0.01 M H$_2$SO$_4$ + 0.001 M MnSO$_4$ for 6 days (Fig. 2a), forming a smooth ligament structure with an average ligament diameter of 45 ± 11 nm. This alloy was also dealloyed potentiostatically in the same solution by driving at -0.11 V vs. a saturated mercury sulfate reference electrode for 14 hours. The ligament structure (Fig. 2b) is the same, but the dimensions are smaller by a factor of 3, with an average ligament diameter of 16 ± 4 nm. Forcibly increasing the dealloying kinetics leads to smaller dimensionality.
Figure 2. Dimensionality is affected by dealloying kinetics. The ligament size changed by a factor of 5 when dealloyed in 0.01 M H$_2$SO$_4$ + 0.001 M MnSO$_4$ by (a) free corrosion for 6 days and by (b) driving potentiostatically for 14 hrs.

One feature unique to dealloyed Mn/Cu which is not seen in other dealloyed systems is the presence of internal cracks. Internal cracking in the monolith is most likely caused during the dealloying process due to coherency stresses at the Cu-Mn$_{0.7}$Cu$_{0.3}$ interface caused by lattice mismatch and a martensitic phase transformation.

Mechanical measurements were performed on one sample that was dealloyed for 8 days in pH 1.3 HCl by free corrosion, and had a ligament diameter of 135 ± 31 nm. A Hysitron triboindentor with a 100 nm Berkovich diamond tip was used to measure the hardness of the nanoporous copper. The values were derived from a total of 60 indents with depths ranging from 250 to 800 nm. The nanoporous copper had a hardness of 160 ± 7 MPa, which is surprisingly close to the bulk value of 170 MPa. The Ashby-Gibson scaling law for foams predicts a yield strength of 16.5 Mpa based on the density, which is nearly an order of magnitude less than measured. The small length scale of the ligaments could be responsible for the discrepancy between the nanoporous Cu measurements and the theoretical predictions of the Ashby-Gibson scaling laws following the work of Greer et al. (3,4).

Figure 3. Mn$_{0.7}$Cu$_{0.3}$ dealloyed in pH 1.3 HCl by free corrosion for 96 hrs. The monolithic structure in (a) contains both intergranular and transgranular fracture surfaces. The smooth surfaces are denser layers of copper formed after Mn segregated to the grain boundary and was etched away. The transgranular fracture shown in (b) contains both (c) smooth bicontinuous ligament structures and (d) rough fractured ligament structures.

References
Novel aerogel synthesis is a core expertise of the NSCL. We are always striving to expand our synthesis capabilities and improve our abilities to predict the properties of these materials.
Novel approaches to the synthesis of various three-dimensional (3D) nanostructures have attracted extensive research efforts for the past decade [1]. This research field is growing rapidly since many advanced nanodevices will eventually require a 3D assembly of nanoblocks into either irregularly or periodically interconnected architectures. Currently, nanoporous (i.e., meso- and microporous) solids are, perhaps, the mostly studied class of 3D nanostructures [1]. A common approach to synthesize semiconducting/insulating nanoporous materials is the sol-gel method, affording for both thin films and monolithic nanoporous solids such as aerogels (AGs), xerogels, and cryogels, with AGs exhibiting the highest porosities [2]. Most previous studies have focused on amorphous SiO$_2$ AGs. However, recent advancements in the sol-gel technology have led to a synthesis of a range of other nonmetallic AGs including oxides of Al, Ti, V, Cr, Fe, Sn, and Ru as well as CdS, CdSe, ZnS, and PbS [2,3].

We have developed a sol-gel synthesis of ultralow-density, high-surface-area nanoporous GeO$_2$ monolithic aerogels. The average density of as-prepared monoliths ($\sim 1 \times 1 \times 1$ cm$^3$ in size) was $\sim 35$ mg cm$^{-3}$ (determined from the dimensions and mass of monolithic samples), which is $\sim 0.8\%$ of the full density GeO$_2$. The morphology of the germania AG is illustrated in a transmission electron microscopy (TEM) image in Fig. 1, showing that the AG skeleton is formed by interconnected elongated nanoligaments, $\sim 15$-$20$ nm in diameter and $\sim 50$-$200$ nm in length (corresponding to aspect ratios of $\sim 3$-$15$). In addition, selected-area diffraction and high-resolution TEM analyses of AGs indicate that the nanoligaments are fully amorphous, with no evidence of the presence of either rutile or hexagonal phase (the other GeO$_2$ phases stable at ambient conditions).

It should be noted that the morphology revealed in Fig. 1 is significantly different from that of most of the other AGs reported in the literature [2,3]. For example, amorphous SiO$_2$ AGs typically possess the so-called “string-of-pearls” morphology, formed by interconnected particles with near spherical shape (i.e., with an aspect ratio close to unity) [2]. The observed difference in microstructure between these two types of materials is likely due to the differences in the reactivity of their respective alkoxide precursors. The extremely rapid hydrolysis of germanium methoxide and subsequent condensation of germanium hydroxide species during the sol-gel reaction leads to the formation of comparatively large, dense colloidal particles with smooth surfaces. Similar observations were reported in the characterization of germania-doped silica aerogels and glasses [4]. As a result, these
germania AGs exhibit surface areas lower than those reported for silica aerogels of equivalent densities. Our BET/BJH nitrogen adsorption/desorption analysis has revealed a BET surface area of 58 m$^2$ g$^{-1}$, an average BJH pore diameter of 15 nm, and a pore volume of 0.2 cm$^3$ g$^{-1}$.

In addition, analysis of soft x-ray absorption near-edge structure (XANES) spectra has revealed that Ge atoms in these AGs are locally in a (distorted due to inhomogeneous broadening associated with the amorphous nature of the material) tetrahedral environment similar to that in hexagonal ($\alpha$-quartz-like) GeO$_2$. These AGs could be used in the fabrication of the next generation devices based on GeO$_2$ nanostructures, such as optical waveguides, charge storage elements in nanoscale memory devices, and optical emitters [5-8]. Moreover, such AGs are excellent candidates for (easily removable/dissolvable) templates for the synthesis of novel nanoporous solids [9].

References

Facile synthesis and electronic structure of high-surface-area SnO₂ aerogels

Tin dioxide (SnO₂) is a wide band gap semiconductor with a room-temperature band gap of ~3.6 eV. It is a prototype transparent conductor [1] and a model system for metal-oxide-based gas sensors [2]. Tremendous current interest in SnO₂ nanostructures has been stimulated by a possibility to develop a new generation of high-performance devices including gas- and bio-sensors, batteries, and catalysts. However, there are few examples in the literature of porous 3D SnO₂ nanostructures. This is not surprising since the solution-based techniques used to prepare 3D SnO₂ nanostructures commonly require highly reactive tin precursors, complex solvent systems, and/or elevated temperatures.

We have successfully synthesized monolithic SnO₂ aerogels using a straightforward sol-gel technique. The synthetic flexibility of the epoxide-initiated gelation process used also presents the opportunity for future systematic studies of SnO₂ nanoarchitectures with the goal of optimizing material properties for specific applications. Our low-density (97% porous), high surface area (383 m²/g) SnO₂ material is comprised of interconnected, randomly oriented crystalline (rutile) SnO₂ nanoparticles ~3-5 nm in size, as illustrated in a transmission electron microscopy (TEM) image in Fig. 1(a). Figures 1(a)–1(c) also show that annealing at temperatures ~400° C has a negligible effect on the average size of nanocrystals. For these annealing conditions, aerogels remain monolithic. However, Fig. 1(d) clearly shows that, during annealing at 550° C, nanoparticles experience agglomeration and faceting. Such an increase in the nanoparticle size up to ~15 nm [Fig. 1(d)] is also accompanied by a collapse of monolithic samples into powders.

Since gas sensor applications of SnO₂ are related to surface electronic properties, we have examined the electronic structure of the SnO₂ aerogel using soft x-ray absorption near-edge structure (XANES) spectroscopy. High-resolution O K-edge and Sn M₃- and M₄,5-edge XANES spectra of monolithic nanocrystalline rutile SnO₂ aerogels with different surface areas (i.e., different surface-to-volume atom fractions) have been compared with spectra of full-density rutile SnO₂ and tetragonal SnO. Spectra have been interpreted based on the electronic densities of states in SnO₂ calculated with both cluster (self-consistent real-space multiple scattering) and band-structure (linear muffin-tin orbital) methods. Results have shown that, in contrast to the currently widely accepted picture, the presence of undercoordinated surface atoms not only affects the Fermi level position but also changes the structure of the conduction band.
by introducing additional Sn-related electronic states close to the conduction band minimum (see Fig. 2). These additional states are due to oxygen deficiency and are attributed to a surface reconstruction of SnO$_2$ nanoparticles forming the aerogel skeleton. Results of this study are important for understanding the physical processes underlying the performance of gas sensors based on SnO$_2$ nanostructures.

Reference


Novel 3D fabrication Techniques

The third theme area for the NSCL is novel 3-dimensional fabrication processes. We have been pursuing interference lithography, expanding 2-dimensional lithography, and focused ion beam (FIB) technology.
Density gradient structure made through proximity field nanopatterning
Seokwoo Jeon, Yun Suk Nam, Jang-Ung Park, John A. Rogers, (University of Illinois, Urbana-Champaign) Robin Miles, Jackie Crawford, Nick Teslich, Alex V. Hamza, (LLNL)

High-resolution, conformable phase masks provide a means to fabricate, in an experimentally simple manner, classes of 3D nanostructures that are technologically important but difficult to generate in other ways. In this approach, light passing through a phase mask that has features of relief comparable in dimension to the wavelength generates a 3D distribution of intensity that exposes a photopolymer film throughout its thickness. Developing this polymer yields a structure in the geometry of the intensity distribution, with feature sizes as small as 50 nm.

**Fig. 1.** Schematic illustration of steps for using a high-resolution conformable, elastomeric phase mask to produce 3D nanostructures. Placing such a mask (Upper Left) on the surface of a solid photopolymer film leads to intimate, conformal contact driven by van der Waals forces (Upper Right). (Upper Left Inset) SEM of the surface of a representative mask with relief features in the geometry of a square array of cylindrical posts with a diameter of 375 nm and a height of 420 nm. (Upper Right Inset) Top-view optical micrograph that shows the progression of a ‘‘wetting’’ front that establishes conformal contact between the mask and the underlying photopolymer. Shining light through the mask while it is in contact with the photopolymer film (Lower Right) generates a complex intensity distribution throughout the thickness of the film (Inset), when suitably coherent light is used. Interaction of the light with the polymer results in crosslinking reactions. Washing away the uncrosslinked polymer yields 3D nanostructures whose geometry is defined by the 3D interference pattern formed during exposure (Lower Left). (Lower Left Inset) SEM of a typical structure. From reference [1].
Fig. 1 shows the procedures to produce 3D nanostructures. All of the necessary optics are built into a single element: a conformable, elastomeric phase mask with features of relief that have dimensions comparable to the optical wavelength (Fig. 1 Upper Left). *Inset* shows an angled view scanning electron micrograph (SEM) of the surface of a phase mask. Placing this type of mask against a solid film (5–15 μm thick, formed by spin casting) of a photopolymer (SU-8, Microchem, Newton, MA) leads to intimate physical contact driven by van der Waals forces. This simple procedure aligns the mask to the surface of the photopolymer with atomic scale precision in the z direction (Fig. 1 Upper Right). Complete contact over several square centimeters requires 1 or 2 sec. Passing light through the mask generates a complex 3D distribution of intensity that exposes certain regions of the photopolymer.

We have used the above technique to fabricate graded density structures with nanometer scale features. If there is negligible adsorption of the light in the photopolymer a uniform 3D structure will develop. If, however, the absorption of the light in the photopolymer is significant, a graded density structure can be produced. Further from the source, the intensity of the light will be decreased and less crosslinking of the photopolymer will occur (see figure 2 for a light intensity map). By exposing the photopolymer with between 30–40 mJ/cm² of 355 nm light through the conformable mask and 150 mm thick glass plate a suitable intensity gradient was generated. A scanning electron micrograph of the resulting structure is shown in figure 3. The density gradient could be controlled from full density (1.2 g·cm⁻³) to 0.18 g·cm⁻³ over distances from 40 to 100 μm.

![Figure 2. Light intensity distribution in the photopolymer in the case of no absorption (left) and with absorption (right). Absorption in the polymer causes a continuous variation in exposure dose with depth. The bottom of the images have full light intensity and the top of the images are 10 μm into the photopolymer.](image)

![Figure 3. (left) scanning electron micrograph of a fractured cross section of a density graded structure on polycarbonate substrate and (right) x-ray micrograph density graded structure on brominated polystyrene substrate. The density graded structure is on the right side of the image.](image)

**References**

Pyramidal Structures for Graded Density Target Material
Robin Miles, Jackie Crawford, Tim Graff, Julie Hamilton, Susan Ratti, Cheryl Stockton
Jerry Britten, Hoang Nguyen, Leslie Summers

One possible method for producing graded density material is to fabricate an array of pyramids or cones in the material as shown in Figure 1. Like an ordered mountain range, the material is fully dense at the base of the pyramids. The fraction of material versus void, and thus the density, changes with height above the base until the material is fully voided at the peaks. This material is useful if the relevant experimental length scale is large compared to the peak-to-peak distance between the pyramids. Two separate methods were used to fabricate such structures in polymeric materials. The first involved creating a mold to cast the polymer and the second involved applying interferometric lithographic techniques directly to photosensitive polymer to create the structures.

Figure 1. Array of pyramidal structures in SU8 polymer

Polymeric pyramidal arrays can be fabricated in a three-step process. In the first step, deep pits are etched in silicon substrates using the deep reactive ion etch (DRIE) Bosch process. Figure 2 shows the results of this process for a variety of holes sizes ranging from 1 to 5 microns. The silicon is then etched using an isotropic etchant to enlarge the pits until they begin to coalesce at the surface of the silicon. In the third step, the etched structures are filled with polymer. The cured polymer structure is released from the mold by etching away the silicon. Figures 3 and 4 depict arrays of pyramids about 8 um peak-to-peak and about 15um high and 8 um peak-to-peak and about 59 um high, respectively. Figure 5 shows the density fraction plot with depth for the material in Figure 4. Reduced peak-to-peak distances could be achieved using anisotropically-etched thick oxide etch masks during the DRIE process. Thick etch masks are required for the longer etch times needed to make the deep structures in silicon and anisotropically etched masking layers are needed for the required resolution.

Figure 2. DRIE holes etched in silicon substrate.

Higher aspect ratio etches could possibly achieved using the Alcatel “sharp” process for which the company claims a 60:1 aspect ratio for 0.5 um diameter holes. The uneven surface of the longer pyramids could be improved using better polymer fill procedures such as a vapor deposition processes. It should also be noted that silicon pyramids can be made directly by over-etching during the isotropic etch.
Interferometric lithographic methods can also be used to create these materials. This technique uses two laser beams to create an interference pattern, a series of light and dark bands, on photosensitive polymer resist. When developed, the photoresist forms a series of peaked structures as shown in Figure 6. The peak-to-peak distance of this material is 4 um and the height if 13 um. The density fraction of this material is shown in Figure 7. This variation is approximately linear up to about 95% full density. The peak-to-peak distance for this structure could be reduced by better matching the emission wavelength of the laser to the sensitivity of the photoresist and by reducing environmental factors such as substrate vibration which “blurs” the exposure.

Furthermore, by overlaying multiple exposures or by combining more than two beams, more complex two-dimensional (2D) structures can be patterned including pyramidal arrays.

In conclusion, several types of polymeric density graded structures have been demonstrated for the sub-10 um pitch under 50 µm high regime. Future improvements would involve processes to reduce the pitch distance for the 50 µm and thicker materials.

References:
A number of LLNL programmatic applications require the ultra-precise application of nanoliter or picoliter quantities of special liquids at specific locations. For instance, the construction of complex laser targets often involves the seamless joining of tiny parts made of unique materials (Fig. 1). This can be accomplished by the use of special adhesives. Traditionally, the application of liquid adhesives to laser targets and other small objects has been done using single camel hairs as paintbrushes. A new approach to precision liquid application is the use of ultrasonic inkjet technology, similar to that used in desktop inkjet printers. Such technology, which can reproduce the finest text, can also be adapted to the precision application of liquids to precise locations.

We are using a combination of commercially available specialty inkjet components, and custom-engineered hardware, to build new equipment that uses ultrasonic inkjet techniques to apply tiny droplets of different liquids to complex parts. In addition to the laser target application described above, the device could be used to apply biochemical solutions to biochips and to print conductive polymers onto flexible substrates. The latter two applications require a very flexible system. Therefore the project goals include the construction of two complete systems, one specialized for target fabrication that can be integrated with existing specialized target assembly equipment, and a more general-purpose system that can be used for many applications, ranging from printing conductive plastics to applying biochemical solutions to sensor devices.

The inkjet techniques used in this project are fundamentally the same as those used to generate high-quality printed material. A typical inkjet device used in the project is shown in Fig. 2.

![Figure 1. Adhesive joining of the hemispherical halves of a typical laser target. Target is shown in (a) and typical application technique is shown schematically in (b).](image1)

![Figure 2. A typical inkjet device used in the project. The “business end” of the device is a tiny glass nozzle that generates droplets as small as ten microns in diameter.](image2)
Before the design and construction of any new hardware, tests were conducted in laboratories at the University of California - Berkeley to verify that the inkjet methods being considered are indeed capable of “printing” individual droplets of custom liquids such as low-viscosity adhesives. These tests involved deposition onto various substrate materials as well as bond lines between small plastic parts. The results confirmed that the method would work. The droplets generated in this way are less than a quarter the width of a human hair. The results of one such test are shown in Fig. 3.

Figure 3. Scanning electron microscope image showing a portion of a large spot array made by depositing individual droplets of low-viscosity adhesive onto a hydrophilic polished glass substrate. Results show that the inkjet method is flexible, precise, and repeatable.

After these successful tests, the work focused on the development of two new systems at LLNL. For the target fabrication system, close cooperation with the target fabrication community was essential. Working closely with target fab engineers and technicians, a system was developed that mates directly to the existing target assembly station, and can be attached and removed as required. The ultrasonic inkjet tip is located on a long probe that allows it to approach a small target being held within the vertical fixturing of the assembly station. A computerized motion controller manipulates the probe, and a special compact microscope mount allows the operator to view the deposition process. The general-purpose system is similar in capability but very different in form, with an open geometry that allows excellent access to a wide range of substrates, and a 2-D computerized linear stage that enables either the precise placement of individual droplets or the large-area printing of complex patterns. The general-purpose system, as completed, is shown in Fig. 4.

Figure 4. The general-purpose ultrasonic inkjet system in the LLNL Microfabrication Laboratory.
Etch and deposition processes for multiple layer targets
Robin Miles, Jackie Crawford, Susan Ratti, Cheryl Stockton, Ron Foreman, James Embree

Etch and deposition techniques were applied to the fabrication of equation-of-state targets. Currently, these targets are assembled by gluing planar layers of different materials together in a stack as shown in Figure 1. Glues tend to introduce unwanted material and voids between the layers. To avoid the use of glue, alternative fabrication methods were considered. To make the structure of Figure 1, it was proposed to etch 1.5 mm wide, 3 mm long, 43 um deep pockets into a 150 um thick quartz wafer, sputter deposit copper into the etched pockets, polish the copper back to the level of the quartz, sputter deposit an aluminum layer, mold-on brominated-polystyrene then evaporate parylene onto the stack and dice the wafer into individual targets.

Unlike much of the literature, the etch revealed preferential etch planes such that a splay mask and pre-etch is required to correctly orient the wafer such that the correct pocket edge is etched vertically. A segment of the wafer with etched pockets is shown in Figure 2. The measured surface roughness for the quartz wet-etch was 220 nm rms. Dry reactive-ion etches are also possible and some preliminary work was done by Alcatel as shown in Figure 3. The etch was limited by using a Ni etch mask that tended to sputter and deposit into the etch area and thus increased the surface roughness of the etched pocket. An anistropically-etched polysilicon mask was suggested for future work.

The first step in the process, the quartz etch was accomplished using a 49% HF etch solution at 45C. While most quartz etching is performed at room temperature, it was found through experiment and through literature [1-3] that etching at elevated temperatures improved surface roughness. The etch mask was a photoresist-coated Cr-Au mask. The photoresist covers pinhole defects in the Cr-Au masking layer.

Figure 1. Equation-of-state targets (layer thicknesses in microns)

Figure 2. Parts exhibiting target fabrication process: 1) quartz wafer with etched pockets 2) pieces of diced quartz wafer with copper in pockets following sputter deposition of copper on wafer and polish 3) aluminum sputter deposition on quartz wafer post copper polish (copper in wells)

During the second step in the process, a 43 um copper layer was sputtered onto the quartz. This copper layer is polished.
until the level of the copper coincides with the top surface of the quartz. Figure 2 shows a diced quartz piece following the polish back procedure such that the copper is filling the etched pocket in the quartz. The polish results in a slight dip (2 um) in the level of the copper versus the quartz such that a machining step instead of a polishing step might be advisable. The thin quartz wafer also tends to cleave during this step due to the stresses of mounting and polishing. Figure 2 also shows a 70 um aluminum layer applied to the wafer following the copper polish.

The polystyrene molded directly to an aluminum- coated substrate exhibited poor adhesion to the aluminum layer and solution of this issue will require research into better adhesion promoters. Thick parylene layers were demonstrated.

In conclusion, the effort to date has demonstrated the feasibility of using etch and direct deposition techniques can be used in the fabrication process of equation-of-state targets.

References:

Two New Rotary Fast Tool Servos and a Rotary/Linear Electromagnetic Actuator
Richard C. Montesanti (LLNL), David L. Trumper (MIT)

This project developed two high bandwidth short-stroke rotary fast tool servos and a hybrid rotary/linear electromagnetic actuator that one of them uses. A fast tool servo (FTS) is a high-speed auxiliary servo axis that is added to a diamond turning machine (ultra-precision lathe) to allow generating free-form non-axisymmetric or textured surfaces on a workpiece. A rotary fast tool servo produces an in-and-out motion of the tool relative to a workpiece by swinging the tool along an arc having a fixed radius. The rotary fast tool servos developed in this project were designed to specifically accommodate diamond turning prescription textured surfaces on small spherical workpieces (diameters in the range of 10 mm or less), and are suitable for generating free-form non-axisymmetric surfaces on similar-sized workpieces. These rotary fast tool servos set new benchmarks for demonstrated closed-loop bandwidth (10 kHz) and tool tip acceleration (400 g).

Figure 1a. The 2 kHz rotary fast tool servo on a diamond turning machine (left), and its rotating element not including the actuator (right).

The first machine, referred to as the 2 kHz rotary fast tool servo (Figure 1a), uses a commercially available moving-magnet galvanometer as the actuator (Lorentz force), and provides proof-of-principles for a flexure bearing, small diamond tool and mounting method, circuit topology for a high bandwidth current-mode amplifier, and control system design. We demonstrate the following closed-loop performance for the 2 kHz rotary fast tool servo: -3dB bandwidth of 2 kHz, 20 g tool tip acceleration at 2 kHz, maximum tool travel of 50µm PP, and tool position noise level of 10 nm PP. The 2 kHz FTS is integrated with a diamond turning machine and used to produce optical quality textured surfaces on the face (Figure 1b) and outside diameter of aluminum workpieces while operating at 2 kHz. The machining tests validate that a rotary-type fast tool servo can be used to produce optical quality surfaces on a spherical workpiece from its pole to its equator.

Figure 1b. Portion of a textured surface that was single-point machined onto the face of a workpiece that was rotating at 480 RPM, using the 2 kHz rotary FTS (left). 3-D surface map of a portion of the surface (right, upper). Profile across the 2.2 micron PV grooves (right, lower). Surface roughness along the grooves is 12 nm rms.

The second machine, referred to as the 10 kHz rotary fast tool servo (Figure 2), incorporates the proof-of-principles from the first machine and is the vehicle for developing the hybrid rotary/linear electromagnetic actuator used in it. The actuator is a normal-stress variable
reluctance machine, and we demonstrate an order of magnitude increase in the peak torque and in the ratio of peak torque to electrical power at the terminals of the actuator, when compared to the actuator used in the 2 kHz FTS. By integrating the tool holder directly to the moving mass of the actuator to form a single rigid body we increase the overall torque-to-inertia ratio for the system and increase the frequency of the first uncoupled-mass resonance. We demonstrate the following closed-loop performance for the 10 kHz rotary fast tool servo: -3dB bandwidth of 10 kHz, 400 g tool tip acceleration at 5 kHz, 870 g tool tip acceleration at 10 kHz (utilizing a stable mechanical resonance), maximum tool travel of 70µm PP, and tool position noise level of 1.4 to 2.5 nm rms (depending on the magnitude of the bias flux used).

Figure 2. The 10 kHz rotary fast tool servo on a diamond turning machine, and the rotor for the fast tool servo with its flexure bearing (inset).

The hybrid rotary/linear electromagnetic actuator is similar to the rotary actuators used to drive a mechanical oscillator at resonance in certain electric engraving heads. The magnetic circuit for the actuator is shown in Figure 3. Our work is distinguished from the prior art by the ability to generate closed-loop arbitrary trajectories for the tool tip. Using a separate current-mode amplifier for each stator half allows us to demonstrate simultaneous closed-loop control of the rotary and linear degrees of freedom that are inherent in this class of actuators. Our work is further distinguished from the prior art by a magnetic circuit that substantially decouples certain magnetic flux paths when a coil is used instead of a permanent magnet to provide the bias magnetic flux. Torque control for the hybrid rotary/linear electromagnetic actuator that we built is independent of force control, but force control requires a torque-generating current to act as an operating point. We describe and compare alternate magnetic circuit topologies that fully decouple torque and force control, and suggest future work that utilizes the linear mode as an active suspension for improving the performance of a predominantly rotary system.

Figure 3. Sketch of the magnetic circuit showing torque and force generation for the actuator that we built for the 10 kHz FTS.
Nano-Barometers: an *in-situ* diagnostic for high pressure experiments

James S. Stölken

The mechanistic understanding of high pressure phenomena requires the capability to probe the local material response at high spatial resolution using experiments with complex loading history. Such experiments rely heavily on computational simulations for the interpretation of local conditions such as temperature and pressure history. The development of an *in-situ* nano-scaled pressure sensor provides a means to assess the quality of these simulations through the direct measurement of local peak pressure and comparison with simulation. The diagnostic developed under this project consists of nano-scale sensors that are imbedded within, or in contact with, the medium to be measured that record the local peak pressure and may be read-out following the experiment using a variety of micro-spectroscopy techniques. The small size of the nano-sensors, combined with low volume fractions, limits the influence of the sensors on the high-pressure phenomena being studied while allowing for high spatial resolution of the peak local pressure. Preliminary work indicates that the fabrication, deployment, and read-out of the nano-scale pressure sensors are possible. We are executing a comprehensive plan to explore the scale dependence, concentration limits, and pressure sensitivity of nano-scale pressure sensors. The final product shall be an *in-situ* nano-scale pressure sensing capability that has been calibrated over a wide range of pressures and a broad range of deformation conditions.

The study of high-pressure phenomena is at the core of many DNT and NIF related programs, with many important applications in the range of a few hundred kilobars, such as fragmentation and spall. Such experiments rely heavily on computational simulations for the interpretation of local conditions such as temperature and pressure history. The development of an *in-situ* nano-scaled pressure sensor provides a means to assess the quality of these simulations through the direct measurement of local peak pressure and comparison with simulation. Such a capability is especially useful in laser-driven experiments with complex wave profiles and non-steady loading (Fig. 1). Potential application to three classes of experiments is envisioned: Quasi-Static Experiments in Bulk Materials, Unsteady Shocks in Bulk Materials, and High Explosives. For a variety of experiments, from gas-gun and laser-driven experiments to Site 300 and NTS U1a test shots, there is a need for an accurate, local measure of material peak pressure.

Figure 1: Computed peak pressure profile due to a laser-driven shock (J. Colvin, LLNL)

The goal of this work is to develop an *in-situ* diagnostic for high-pressure experiments capable of providing local peak pressure information at high resolution (<1 micron) and over a broad range of pressure (30 – 300...
kbar). Key issues to be addressed shall include calibration and sensitivity analysis of the nano-sensors to both quasi-static and shock loading conditions. Major goals of the proposed research are to quantify the extent of pressure induced changes in the sensor material, determine their dependence on sensor size, and establish the sensitivity of pressure induced structural changes to static loading.

In this study a key question regarding the existence and nature of the densification mechanism in silica nano-particles has been explored. The issue was whether or not the densification phenomena observed in bulk silica occurred in nano-particles. Since the success of the entire project is predicated upon this, it was crucial to experimentally verify this assertion. The results of our initial series of Raman spectroscopy and diamond anvil experiments on silica nano-particles are shown in Figs. 2 and 3. The internally oxidized Cu sample containing the embedded-silica-sensor particles is shown in Fig. 4. The permanent shift in the Raman spectra is clearly visible in Fig. 2, consistent with the published results in bulk silica glass. To the best of our knowledge, this is the first such measurement in nano-particles as a function of particle size. Not unexpected is the dependence of the Raman shift upon the particle size, a key research question to be addressed by this project. Note that each experimental point represents an entire sequence of spectra taken upon loading and unloading of each sample. The spectra shown in Fig. 3 correspond to the highest pressure data-point for the 1.2 micron particles and summarize the results of 105 individual spectral measurements.

![Figure 2: Permanent Shift in Raman Spectra as function of particle size and peak pressure (A. Goncharov, LLNL).](image)

![Figure 3: Raman Spectra as function of pressure for 1.2 micron silica particle. (A. Goncharov, LLNL).](image)

![Figure 4: Sub-micron silica sensors embedded in a copper matrix (M. Kumar, LLNL).](image)
Photolithographically Patterned Polymer Layers for Graded Density Material
Robin Miles, Jackie Crawford, Julie Hamilton, Susan Ratti, Cheryl Stockton

Graded density polymer structures can be fabricated by stacking and bonding individual sheets of photolithographically patterned polymers. Each sheet of photosensitive polymer material can be patterned to create voids of specified sizes corresponding to the required density for that sheet. Sheets of polymer which are 88% dense have arrays of small holes in them. The holes in 75% dense material are twice the area of those in the 88% dense material. The holes in the 50% density sheets are twice the area of the holes in the 75% material. Sheets of 25% and 12% density are more voided than material. Figure 1 shows pixels for these patterns. When these sheets are bonded, the result is a graded density material.

![Figure 1. Pixel patterns for various density layers (light areas become voids).](image)

Prototype graded density structures were built using photosensitive SU8 epoxy. To make these structures, films of SU8 epoxy were spun on silicon wafers to a thickness of about 10 μm. The photosensitive material was photolithographically patterned and developed.

![Figure 2. 75% dense layer.](image)

Figure 2 shows patterned and developed polymer for a 75% filled layer. The silicon backing material was removed by etching the silicon using KOH. The individual layers were coated with 120 nm parylene C for use as a thin, conformal adhesive layer to bond the layers together. The layers were stacked on a specially-made fixture. Figure 3 shows two layers stacked prior to bonding. The SU8 film is translucent so the bottom layer can be seen through the upper layer. The less voided material with small holes sits beneath the more voided layer with larger holes. The stack is compressed and heated to 300°C for about 1 hr to bond the stack. Figure 4 shows a three layer bonded structure which has been cleaved to reveal the bonds. The pixel size in this structure is
about 8 um in length and the layer thickness is about 12 um. Smaller pixel sizes could be achieved either by using thinner layers or using a more collimated illumination source. The stacking procedure for thinner sheets would be altered such that each layer would be bonded separately while still attached to the silicon handle chip to facilitate handling of the thin polymer film. After bonding of each layer, the silicon handle would be removed.

![Figure 3. Two layers stacked.](image)

In conclusion, prototype structures suggest that stacking and bonding sheets of photolithographically patterned polymer can be used for producing graded density materials.

![Figure 4. Three layers stacked and bonded.](image)

References:

Focused Ion Beam (FIB) Technology for Inertial Confinement Fusion  
Nick Teslich, Richard Seugling, Warren Moberlychan, Alex Hamza (LLNL) and Heather Wilkens (GA)

Inertial Confinement Fusion (ICF) targets require micrometer scale structures attached to spherical shells that are ~2 mm in diameter and 100 or more micron thick. We are developing technologies that can be used to attach or grow a filltube for the supply of hydrogen gas to the interior of the capsule. The critical geometry consists of a counterbore 12 µm in diameter and 20 µm deep which has to be concentric to laser drilled hole to ± 1.0 µm. In the attachment process the counterbore will then receive a 10 µm diameter glass tube.

The main items to be addressed in initial testing for counter-boring are:
1) Etching rate of Be counter-bore
2) Smoothness of surface and of side-walls, taper, bottom geometry and aspect ratio
3) Damage to substrate (artifacts, hole clogging, re-deposition, beam damage)
4) Ability to automate (reproducibility, robustness, interface with prior and subsequent processes, fixturing, drift, surface charging).

Balancing the requirements of smooth surfaces and side walls with minimizing damage and re-deposition led to the selection of a 7nA beam current, with each hole taking just over 30 minutes to create. The side walls were visibly smoother with less tapering at the upper rim than with higher currents. The diameter of the hole at 20µm depth was 8µm. In general, the taper improved over higher ion currents. There was less beam damage and bottom geometry was improved. At lower currents beam drift became an issue, because the etch rate was reduced to unacceptable levels.

The figure 2 shows a counter-bore over a laser drilled hole in a Be capsule. The ion beam etch parameters were 14.5µm-diameter x 17µm-deep. The counter bore used an outer-to-inner scan, ion beam dwell time of 1.0µs per spot and 50% overlap of the ion beam spots. Producing exact depths and reproducible etch rates are remaining difficulties due to the fluctuation of the geometry of the laser-drilled hole.

Preliminary tests show that the etch rate of a 20µm-deep hole is >30% faster with a pre-existing laser hole. Fixtures for holding the capsules will improve concentricity between the laser hole and FIB counter-bore.

The final steps for production are to develop a repeatable process and computer automation.
The success of automation is a function of reproducibility of the laser drilled holes and a standard fixture common for both the laser and the FIB. Scripting and image recognition programs can then be written to automate the counter-bore process.

The ability to grow a fill tube to interface with existing glass tube technology for means of filling target capsules using FIB technology is being explored. Growing a fill tube may be able to keep the critical mass defect at the capsule to a smaller level. The FIB has the capability to deposit material by inserting a micro-needle 200 µm from the surface of the sample and injecting a gas. This gas reacts with focused ions patterned on the surface to create a deposition rather than the traditional etching and sputtering processes commonly performed by the FIB. Currently, the FIB at LLNL has three types of gases for deposition Pt, C and TEOS.

The initial experiment used C-deposition circularly patterned over a counter-bore. The initial results are promising, showing a substantial growth rate as seen in Fig 1.

C-deposition was performed over existing FIB counter-bores 12µm-diameter x 20µm-deep as shown in Fig 2. An ion current of 1 nA was explored for the initial test producing a growth rate of ~.16µm/min. The growth of the fill tube including the 20µm counter-bore was ~ 45µm and took ~4.5hrs.

The measurements at the top of the C-deposition tube was consistent with design showing the internal diameter of the hole ~5.8µm and outside diameter ~10.7µm.

Unknown factors in the fill tube growth techniques are gas stability, chamber vacuum stability and ion beam stability when depositing over large blocks of time.

FIB based tube growth shows potential to facilitate filling target capsules. Further investigation into tube strength, sealing capability and possible clogging or flow issues is needed. The initial work was performed to demonstrate the capabilities of the FIB for NIF target fabrication and as part of ongoing and future work utilizing FIB technologies.
This project advanced the science of surface bonding in order to enhance the functionality demanded by target fabrication requirements, as well as similar needs in other fields of importance to LLNL. We have developed and demonstrated a very powerful capability, i.e. “single molecule force spectroscopy,” that allows us to determine the strength of individual chemical bonds. In addition, this tool is scalable, permitting the measurement of much larger force interactions as discussed below. Our progress reflects our current focus on understanding the fundamental nature of bonding by exploiting adhesion processes found in chemical and biological systems.

![Figure 1. A schematic of the rupture configurations of two thiolate bonds- a single or 'isolated" sulphur-gold bond and a double or "grouped" sulphur-gold bond. Surprisingly, the measured rupture force for the isolated bond was three times greater than the force required to rupture a grouped bond. This finding correlates with a mechanism for grouped thiol desorption that includes the lowering of the barrier to desorption through the formation of disulfide bonds. (Ref 1.)](image1)

![Figure 2.. Histograms of multivalent rupture forces measured between a single protein and multiple receptors. The inset shows the results from a single experiment. The main histogram shows the results from multiple experiments. The main finding is that multivalency does not scale linearly (e.g. two bonds are not twice as strong as one,) which has important implications for how biological organisms (especially bacteria and viruses) mediate adhesion and subsequent infection through multivalent bonds. (Ref. 2)](image2)

References


The fourth theme area for the NSCL is nondestructive evaluation on the mesoscale. We have invested in x-ray and acoustic probes.
Phase Effects on Mesoscale Object X-ray Attenuation Radiographs

H. E. Martz, Jr., M. B. Aufderheide, A. Barty, S. Hau-Riege, S. K. Lehman, B. J. Kozioziemski, and D. J. Schneberk

Digital x-ray radiography and computed tomography methods are commonly used to characterize mesoscale objects (mm size objects with µm size features). However the ability of these methods to provide high spatial resolution images is dependent, in part, on object recovery algorithms that account for phase effects [1]. The objective of this work is the development and validation of algorithms to model phase-contrast effects observed in x-ray radiographic systems, and to use these algorithms for quantitative object recovery. This work has three distinct tasks. First, we are modifying HADES [2,3] to model x-ray phase contrast and are investigating whether multislice techniques within the object are needed to fully capture the physics seen in x-ray data. Second, we are developing object recovery approaches. Third, we are validating these simulations against x-ray systems using well-known objects. At the end of this R&D, we will have a set of validated x-ray forward modeling codes including the effects of phase and an understanding of the current object recovery methods limitations.

In the past year, we have fully integrated the Fresnel-Kirchoff diffraction theory into HADES modeling. This required an upgrade of HADES' calls to the FFTW¹ fast Fourier transform library. This work is now complete. In addition, we have merged into HADES the LBNL photoelectric absorption and phase cross sections with the LLNL Evaluated Photon Data Library cross sections for Compton and Rayleigh scattering, as well as Pair Production. Compton Scattering becomes a sizeable part of the absorption cross section for low-atomic-number materials at high x-ray energies. Representative results from the new HADES code are shown in Figure 1.

The resolution of x-ray images has improved to the point that spatial resolution and object dimensions could theoretically result in the wave diffraction effects within the object becoming significant. We studied this possibility numerically using four simulation codes that incorporate x-ray phase effects. We refer to them as (1) The paraxial approximation multi-slice simulation code; (2) A Kirchoff propagation simulation code; (3) A Mie type analytical simulation code [4]; and (4) HADES. The paraxial approximation code with and without a multislice method and the Kirchoff propagation code were used to model at worst-case x-ray energies of ~8 keV and compared these results to empirical data. The conclusion, based upon the results of the validated simulation codes, is that diffraction effects within the object are insignificant for >= 8 keV x-rays data with ~1-µm spatial resolution and for objects up to 10 mm (Figure 2).

Figure 1 HADES simulated radiographs of a cylindrical reference standard without (a) and with (b) x-ray phase. Note x-ray phase effects create the well known bright and dark edges.

A number of approaches have been developed for recovering phase from mesoscale radiographs. A certain class of phase recovery techniques employs differential equation solvers (Multi-Grid techniques) to solve for the electron density. We have implemented the most straightforward technique, which applies to the case of weak absorption and uniform irradiance. We have applied Multi-Grid techniques to both synchrotron and non-synchrotron data. An example of results for a point-projection non-synchrotron system (Xradia Micro-XCT) is shown in Figure 3. Comparisons with simulated data have shown

¹ Fastest Fourier Transform of the West
the range of these techniques to be limited to cases of 90% transmission or better for simple geometric objects. Most of our data are on order of 20% transmission for objects with complex geometry and thus this object recovery method is not very useful for most of our data. Furthermore, we have found these techniques to be sensitive to clutter in the scintillator and small aberrations in the optics used to couple the light from an x-ray scintillator to a CCD camera.

Figure 2. Lineout plots of the single (a) and double (b) C fiber projections. The measured data (open circles) were collected by a Cu-anode source and a direct detection CCD camera.[5] The simulated straight ray (red curve) and the multi-slice (blue curve) projections have been convolved with a single Gaussian line-spread function with a Gaussian sigma value of 3.6 and 4.0 for the single and double fiber data, respectively. Note the very good agreement between both simulated results and the empirical data.

The ‘multi-slice’ phantom was fabricated to contain either 6-µm outer-diameter carbon fibers or 4-µm outer-diameter tungsten wires in various pre-selected configurations. The fibers or wires are attached to a base and slide that is adjustable in separation length from 2 to 10.2 mm. Three 5-µm carbon fibers were inserted into the multi-slice phantom and the phantom was oriented such that the fibers were vertical in the digital radiographs [see Figure 3(a)] and rotation could be used to align the two carbon fibers that were separated by 10.2 mm.

Figure 3 Digital radiograph of the two non-aligned C fibers acquired at 99 kV and 41 µA and pixel size of 0.6 µm at the object center (a). Electron density (related to x-ray phase) results (b) from application of the weak absorption and uniform irradiance method on the digital radiograph shown in (a).

References
Non-destructive characterization of density, pore size and particle size fluctuations
Tony van Buuren, John Kinney, Trevor Willey, and Rob Muelenberg

We are attempting to measure how the structure of highly porous metal and metal oxide foams changes with temperature, pressure, and surface environment. We are studying how these porous materials deform with mechanical or thermal stresses by using a combination of small angle x-ray scattering (SAXS) and high-resolution synchrotron radiation computed tomography (SRCT). SAXS is an established technique, to study the morphology of polymers, ceramics, and biomaterials; here, it has been extended to probe structural inhomogeneities on the order of 1 nm to 1000 nm in nanoporous media. SRCT, which was pioneered at LLNL, will be used to quantify density fluctuations in the foams at length scales approaching 100 nm. Input from both SAXS and SRCT is used to generate microstructural models of the foams for analysis with finite element modeling.

The ultra-small angle x-ray scattering, data shown below, was performed on a 100mg/cc tantalum oxide foam. The scattering as a function of wave vector, \( Q \), is indicative of scattering from a collection of rod-like structures with a rough surface (Figure 1a). A Kratky analysis of the data, in turn, is suggestive of a branch-chained structure with a well defined unit cell (Figure 1b). The radius of gyration of the rod-like structures was approximately 12.5 nm, and is consistent with a random orientation of rod-like structures 40 nm in length.

In order to get a complete understanding of the three-dimensional structure of the foam, a series of images were obtained using a lensless diffraction technique. A complete reconstruction of a 2 micron particle of the foam is shown in Figure 2a. At small length scales (i.e., 500nm), the structure appears to be anisotropic, with most mass oriented in plane. This is consistent with some evidence of alignment in the diffraction patterns. This is an important new result, for it has been assumed that these metal oxide aerogels are isotropic at all length scales; the distance over which this anisotropy persists must still be established.

Figure 1: a) Left image showing the scattering intensity as a function of the wave vector over 3-orders of magnitude in \( Q \). Shape factors and slope of the Porod region are characteristic of a rod-like structure with rough surfaces. b) Right graph showing Kratky analysis. Results are consistent with a branch-chained structure of fairly uniform cell size.
The lensless images have provided valuable information regarding the three-dimensional architecture of the foam lattice. We are now confident that the USAXS data is providing us details about the cell size in these foams from 10-1000nm.

The elastic constants of the ultra-low density tantalum oxide foams have not been measured. Therefore, we used finite-element simulation to estimate the apparent elastic modulus of the foam structures; the mesh was a high-fidelity reproduction of the three-dimensional foam structure determined from the lensless images. Simulations were performed with NIKE3D using periodic boundary conditions. An apparent Young’s modulus (defined as $E_s/E_b$, where $E_s$ is the modulus of the structure and $E_b$ is the modulus of full-density tantalum oxide) of $1.2 \times 10^{-4}$ was determined from the finite element simulation. This is less than the value of $7.5 \times 10^{-3}$ predicted from theory. However, theoretical models assume that all of the mass is distributed within beams of uniform shape; the three-dimensional images indicate that a large amount of the mass might be segregated at the nodes.

Using connectivity destroying operations, we established that, for the 100mg/cc tantalum oxide foam, approximately 85 percent of the mass was confined to the nodes. Correcting the scaling laws for the reduced apparent mass lowered the theoretical estimate to $1.7 \times 10^{-4}$, in excellent agreement with the simulations. We hypothesize that the theoretical scaling laws based on uniformity of the mass distributions can be extended to ultra-low densities when the non-uniform mass distribution is included.

![Figure 2: a) 3D isosurface of lensless image of Ta2O5 foam particle (size of particle ~2 microns in max extent). b) High-resolution rendering of 500nm cube (Fig. 2a in collaboration with H. Chapman, A. Barty, S. Marchesini)](image)

The engineering stress-strain behavior of a 500nm cube of 100mg/cc tantalum foam obtained from nonlinear finite element simulations of a high fidelity mesh derived from the three-dimensional lensless images. The apparent modulus is approximately 16.5MPa, and the structural stiffness begins to drop immediately as the foam deforms in bending. The modulus is more than an order of magnitude lower than predicted by theoretical models of open cell foams, indicating that at extremely low density the foams do not behave as expected.
Acoustic Characterization of Mesoscale Objects
Diane Chinn, Robert Huber, David Chambers, Todd Murray (Boston University), James Spicer (The Johns Hopkins University)

Mesoscience is an emerging area of science and engineering that focuses on the study of materials with dimensions, features and structures that range from a few millimeters down to a few micrometers. Mesoscale objects typically have embedded features that require characterization with resolution on the order of a few micrometers. Mesoscale nondestructive characterization technologies are required that can (1) penetrate into or through a few millimeters of diverse materials and (2) provide spatial resolutions of about a micrometer. An acoustic technique is attractive because it offers high sensitivity to features such as thickness and interface quality that are important to mesoscale objects. In addition to the resolution requirements, many mesoscale objects require a non-contact technique to avoid damaging fragile surfaces.

This research will achieve micrometer resolution characterization by extending the range of laser-acoustic testing (Fig. 1) to GHz frequencies. Materials and the geometry of components used in most LLNL mesoscale objects necessitate the use of a non-contacting technique at frequencies from 100 MHz to 10 GHz. This frequency range is required to acoustically characterize features from 5 to 0.5 µm in size. In order to be applicable to mesoscale objects, the GHz acoustic waves must propagate sufficient distances into materials of interest – for LLNL applications, mesoscale structures are on the order of 25 - 200 µm thick.

Figure 1. Laser ultrasound uses a pulsed laser as a source to generate acoustic waves and a laser interferometer to detect acoustic waves. The source and receiver can be on the same side (as shown) or on opposite sides of the object. The acoustic wave travels through the object before it is detected. Use of a pulsed laser gives temporal resolution to the detected signal.

Major accomplishments to date are 1) Determination of ultrasonic velocity and attenuation in several Laboratory-important materials at frequencies ranging from 500 MHz to 1 GHz for thermoelastic and ablative wave generation, 2) Validation of acoustic and laser-acoustic models with experimental data and 3) Assembly of a prototype GHz laser-UT system (Fig. 3). The prototype system was assembled at Boston University and was transferred to LLNL in FY05. In Summer 2005, a graduate student from Boston University worked at LLNL to assemble, calibrate and operate the system. A paper describing this mesoscale acoustic research was presented at “Review of Progress in Quantitative Nondestructive Evaluation, 2005”.

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Our work to date has enabled new research on acoustic wave generation, scattering mechanisms and interface characterization in the GHz regime. Future work is planned in 3 specific areas. 1) GHz laser-acoustic wave generation will be studied with advanced laser-interaction models. Identifying the thermoelastic – ablative threshold for materials through modeling is important to applications requiring “sub-ablative” wave generation. 2) GHz wave propagation and scattering mechanisms will be studied. Anisotropy effects resulting from columnar grains and scattering from microporosity in aerogels are features expected in unique LLNL materials. 3) Capabilities of GHz characterization of interfaces will be studied using models and experiment. Interfaces such as repeating structures and gaps sized on the order of microns are two areas where performance of GHz waves is unknown.

References


Radiation Detection Materials

Development in radiation detection materials has been relatively stagnant for the past decade. The past decade’s advances in nanoscience for the synthesis of materials make the radiation detection materials field ripe for progress from the application of nanoscience. The NSCL began a fledgling effort in FY05 on radiation detection materials, which we hope to nurture and grow in the future.
Biomimetic approaches to growing radiation materials

Chris A. Orme

A recent Homeland Security task force identified the need to develop new materials for high-resolution gamma ray spectrometers as one of the nation’s top priorities. As a result, LLNL is currently motivated to strengthen its crystal growth capabilities to enable the synthesis of large, high quality crystals used in radiation detection. Germanium detectors, which are the current “gold standard”, require cryogenic cooling and consequently are expensive and difficult to operate. New materials that can be operated at room temperature, such as high-Z, compound semi-conductors are particularly intriguing as potential replacement materials due to their tunable bandgap energy, which can be designed for specific applications. The challenge is in growing these materials with sufficient size and low defect density. The objective of this work is to use novel crystallization techniques to: a) grow larger, less-defective crystals and b) to grow patterned crystals for more efficient detector schemes.

**Improving crystal growth methodologies using a biomimetic approach**: Because the compound semi-conductor materials are difficult to grow using standard crystal growth techniques, this work looked for inspiration from biological systems that routinely grow high-purity crystalline materials in “dirty” environments.

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![Diagram showing the basic steps to create micro-patterned crystals.](image)

**Figure 1.** Diagram showing the basic steps to create micro-patterned crystals. a) A substrate is prepared that inhibits spontaneous nucleation using a disordered, low surface energy layer. One region is given a favorable chemistry to initiate nucleation. b) A lithographically patterned template is brought in contact with the surface. The pillars of the template have a spacing of approximately an impurity diffusion length, DL, (tens of microns for ions in water). c) Adding a supersaturated solution allows crystallization to initiate at the array with favorable nucleation chemistry and to propagate out from this point. The pillars act as getters for impurities and water allowing the crystals to grow around these features without being poisoned. d) A single crystal with a pattern of holes results after the removal of the template.

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Organisms often build intricate centimeter-scale, crystalline materials with interesting shapes and micron-scale features. Recent work on the Brittle Star[1] has shown that these features can be reproduced by applying sound crystal growth principals with a novel crystallizer geometry.

Aizenberg et al. [1] have found that they can increase the size of crystals by three orders of magnitude by carefully controlling the crystallizing set-up to incorporate the following principles (figure 1):

1. Prevent spontaneous nucleation at random sites. This can be accomplished
by ensure that the crystallizing vessel is chemically modified with a disordered, low surface energy layer that discourages nucleation.

2. Initiate nucleation in one region by using a favorable chemistry or epitaxial fit.

3. Create “getters” for impurities with an optimal spacing of approximately one diffusion length. In two-dimensions this can be accomplished with lithographically patterned silicon pillars placed within the crystallizing solution. In three-dimensions this can be accomplished using molds made from laser interference lithography.

We adapted this approach to the growth of lead iodide. Lead iodide is a high Z material with low resistivity that can be used both as semi-conducting slab detector and as a scintillator. However, PbI₂ has very low electron and hole mobilities, presumably caused by impurities within the material. It is thus important to find methods that reduce impurity levels and to understand which solution impurities incorporate and cause defects within the crystal.

The first step in such a study is to determine the appropriate solution environments for growth. Atomic force microscopy (AFM) provides a very sensitive and quantitative means of determining how the solution state affects crystal growth kinetics. Figure 2 illustrates our results where millimeter scale single crystals (figure 2a) serve as substrates for in situ AFM studies (figure 2b). The atomic steps emerging from a dislocation source display the underlying crystal symmetry, as shown in the molecular model (figure 2c), and have step velocities that reflect the solution ionic concentrations. Because step velocities change in characteristic ways due to impurity interactions, these AFM studies lay the foundation for future studies that will determine how impurities interact with the growing steps and affect growth at the atomic level.

In parallel experiments, suitable solutions were used with a crystallizer geometry similar to Figure 1 but with an electrochemical potential applied to a lead substrate. An integral aspect of the Aizenberg technique is the creation of a stable, yet highly supersaturated solution near the substrate. In our application we use electrochemical drive as a means of controlling the lead concentration in a controlled manner. In preliminary experiments we were able to create patterned thin films (figure 3). For future work we have designed an electrochemical cell with a more ideal electric field configuration and that will allow greater solution flow to allow thicker materials to be grown.

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