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Changes in the Morphology of Si <111> Surfaces Under High-Temperature, Ultra-High-Vacuum Annealing Applications

CNF Project # 317-87
Principal Investigator: Jack M. Blakely

Abstract:
This research project involves analyzing the processes that take place on the Si <111> surface under high-temperature, ultra-high-vacuum (UHV) annealing. Atomically flat surfaces can be obtained by high-temperature annealing in UHV of specially patterned silicon samples according to a procedure developed previously [1]. Normally, many hours of high temperature anneal and slow cooling is required in order to obtain large atomically flat areas. For this project, we investigated the effect of short time annealing (~ 5 minutes) on the silicon surface evolution. Different annealing times and temperatures result in various atomic step distributions. The surface morphology was analyzed utilizing AFM. As an application, we used the annealed silicon samples as substrates for pentacene deposition. Due to the polycrystalline structure of the pentacene film, there is significant scattering of charge carriers at the grain boundaries. Using atomic steps as preferential sites for nucleation, we are working to find the proper growth conditions for azimuthal alignment of the pentacene crystals so that only small angle boundaries are present. In this way, the average mobility of the charge carriers in the pentacene film should be greatly enhanced.

Summary:
Using standard photolithography techniques, various geometric patterns, with dimensions ranging from 10 to 120 µm, were transferred to the wafers in form of ~ 1 µm deep craters. A temperature gradient was intentionally induced by deliberately clamping the sample tighter on the lower side so that we could investigate the influence of a range of temperatures on the same sample. The difference in temperature between the hottest and the coldest areas on the sample was about 100°C. Several other samples were uniformly heated using various annealing temperatures and short annealing times (1-15 mins).

We measured the root mean square (rms) roughness of the surface in unpatterned regions along a vertical line in the middle of the active part of the sample [2], where the temperature gradient was approximately constant. The value of the roughness was obtained from 5 x 5 µm AFM scans, each scan being 0.4 mm apart. Before annealing, the rms roughness of the surface was 0.88 nm. Towards the lower edge of the sample, where the temperature was high enough, the surface succeeds to reach a thermodynamically stable structure of steps and flat terraces even after such a short annealing time. On the upper side of the sample, where the temperature was lower, the terraces do not develop completely. The measured roughness becomes about four times bigger than the starting surface roughness and then drops. Increased roughness of the surface can be explained by the mechanism known in thin film growth as Ostwald ripening. The atoms from the surface of smaller and sharper irregularities have a higher chemical potential than those of larger clusters. As a result of surface transport, smaller clusters will shrink and disappear while larger clusters coarsen. In this process, the measured roughness reaches a maximum under the conditions where enough larger clusters exist. At higher temperature, even the largest clusters start to shrink and flat terraces become easily visible. At lower temperatures, many small islands exist on the surface instead of fewer bigger ones and, as a result, the measured roughness decreases, but it is still higher than the starting roughness.

Another phenomenon analyzed was the process of ridge formation at the edge of mesas and trench formation at the bottom edge of craters. Previously reported by former group members [3], we observed that these structures form even before the silicon surface reaches the thermodynamic equilibrium. As a consequence, surfaces with low step density can be engineered on top of mesas structures.

Finally, some of the samples were used as substrates for pentacene deposition. Pentacene deposition was performed using the deposition facility in Professor Malliaras’ group by the undergraduate student Jing-Chih Michael Hsu. Different substrate temperatures, in general in the 100-130°C range were investigated. The preliminary results show that atomic steps of height 2-3 times the <111> interplanar separation and at least 2-3 µm apart constitute the best silicon substrate for the pentacene crystals to nucleate primarily along the steps. Substrates other than Si, such as sapphire (0001) are being considered.

References:
Changes in the Morphology of Si <111> Surfaces Under High-Temperature, Ultra-High-Vacuum Annealing Applications

CNF Project # 317-87  
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- Atomically flat surface regions are obtained by heating patterned samples in ultra-high vacuum chamber.
- Surface roughness was measured on non-uniform annealed samples.
- A non-monotonic variation in the surface roughness was observed in the first stages of UHV annealing.
- Trench formation at crater borders and ridge development at the edge of mesas was observed even in these first stages of UHV annealing.
- Under proper conditions, pentacene crystals grow along atomic steps.

Figure 1, top left: AFM scan over a large area (60 x 60 µm), showing a crater and the surrounding, stepped region; the surface became atomically flat only in the upper right corner. Some islands formed as a result of surface ripening can still be observed in the middle of the crater and in the left side of the image.

Figure 2, above: Surface roughness changes from the lower (high temperature) to upper side of the sample (lower temperature) going through a maximum.

Figure 3, below left: Monolayer high islands of pentacene crystals aligned along the silicon steps.
Thin Film Nucleation and Growth using Energetic Neutral Species

CNF Project # 459-92
Principal Investigator: James R. Engstrom

Introduction:
The deposition and growth of organic materials for applications in electronics and photonics differs fundamentally from that of more conventional inorganic materials such as metals, semiconductors and oxides. A key difference involves the presence of strong covalent and ionic bonding in the latter class of materials, whereas organic materials are often bound by rather weak dispersion (van der Waals) forces. In this project, we have used supersonic molecular beams as sources for film deposition, in particular, for the deposition of thin films of pentacene, an organic semiconductor.

Summary:
Pentacene is a promising candidate for applications in organic thin-film electronics owing to the ability to form highly ordered thin films near room temperature with excellent electrical transport properties [1,2]. Pentacene, which possesses a very low vapor pressure, presents a number of experimental challenges that must be overcome in order to generate energy tunable beams. First, we designed an in-vacuum evaporator heatable to 200-300°C to provide enough flux for supersonic molecular beams. Next, using time-of-flight quadrupole mass spectrometry, we characterized supersonic molecular beams of pentacene generated using carrier gases of N₂, He and H₂. With these carrier gases, we were able to obtain kinetic energies over the range of Eᵢ = 1.4-10.6 eV whereas incident molecular fluxes were on the order of 10⁻¹⁵ molecules·cm⁻²·s⁻¹ [3]. We find that beam energy affects a number of phenomena, namely nucleation in the monolayer regime, and both the kinetics of thin film deposition and the microstructure in the multilayer regime. Closer examination of the data indicates that the deposition rate in the monolayer regime is determined by the trapping probability of pentacene [3], which decreases with increasing energy. However, in this same regime the trapping probability is found to decrease with more glancing angles of incidence, a result inconsistent with so-called normal energy scaling. In the multilayer regime, trapping probability also decreases with increasing incident energy, but does so at a rate less than that observed in the submonolayer regime. In addition, grain size of multilayer pentacene films is found to increase with increasing incident energy at normal incidence. These results demonstrate that the morphological evolution of organic thin films can be modified substantially at high incident kinetic energies. The nucleation and growth of pentacene on silicon dioxide surfaces modified with hexamethyldisilazane, HN[Si(CH₃)₃]₂, has also been examined [4]. Similar to growth on clean SiO₂ surfaces, the rate of deposition at a fixed incident flux decreases with increasing kinetic energy of the incident pentacene, indicative of trapping mediated adsorption. Unlike clean, unmodified SiO₂ surfaces, however, growth on the modified surface exhibits the characteristics of heterogeneous nucleation, where the maximum island density is independent of the deposition rate. Deposition in the sub-monolayer regime involves island growth, except that on the modified surface the islands are two molecules high, unlike the one molecule high islands observed on clean SiO₂.

We have also fabricated organic thin film transistors (OTFTs) with these pentacene films with gold top contacts on bare thermal SiO₂ and hexamethyldisilizane (HMDS) coated SiO₂ substrates to understand the relationship between performance characteristics of organic thin film transistors (OTFTs), film microstructure and film-dielectric interface properties. We find that with increasing incident energy of pentacene molecules, the grains get larger and hence the field effect mobility obtained for the corresponding OTFTs increases. In addition, the devices with HMDS primed SiO₂ showed improved performance characteristics with respect to bare thermal SiO₂ owing to reduced trapping at the semiconductor-dielectric interface.

References:
Thin Film Nucleation and Growth using Energetic Neutral Species

CNF Project # 459-92
Principal Investigator: James R. Engstrom
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- Pentacene thin films have been deposited using energetic supersonic molecular beams.
- Incident energy of pentacene molecules strongly influences nucleation, film deposition rate and thin film microstructure.
- Organic thin film transistors fabricated from these pentacene films show promising performance characteristics.

Figure 1: AFMs of pentacene on SiO$_2$ surfaces modified with HMDS as a function of exposure to the supersonic beam ($E_i = 6.7$ eV, normal incidence). In each case the field of view is $5 \times 5$ $\mu$m$^2$. Also shown in the bottom right corner is a micrograph of pentacene on clean SiO$_2$ for otherwise identical deposition conditions and an exposure of 75 s.

Figure 2: Occupancy of the first and second monolayers of pentacene as a function of total amount of material deposited on clean SiO$_2$ (lower panel) and SiO$_2$ modified with HMDS (upper panel). Also shown are examples of two histograms that were used to generate the data that is displayed in the figure.
Low Heat Capacity Substrates for Calorimetry Measurements

CNF Project # 522-94
Principal Investigator: Leslie H. Allen

Abstract:
Our group focuses on developing thermal analysis characterization techniques and instruments for thin film material, nanometer scale particles of metals, polymers and nanoliter volumes of proteins [1-9]. The development of the sensing devices for such a characterization technique-NanoDSC-makes use of MEMS fabrication [4,5] techniques using Si-N membranes. A variety of sample configurations can be used including vacuum-deposited, spin-cast, or growth via liquid solution. A variety of materials phenomenon which occurs at the nanometer length scale have been investigated, such as the size-dependence melting point depression and magic number sizes in metal nanoparticles [1,2,8], order-disorder transitions of self-assembled monolayers of alkanethiols (SAMS) [6], and thickness dependence of glass transition in polymers [3,7]. In this summary report, we discuss work on two topics: (1) heat capacity measurements of thin film polymers [7], and (2) the unusual melting characteristics of bismuth nanoparticles [8].

Summary:
One particular size-dependent materials phenomenon which occurs at the nanometer length scale is the thermodynamic properties of ultra-thin polymer films. Shifts in the glass transition temperature $T_g$ (from bulk values) have been reported for nanometer films. Currently, there is a lack of consensus among various experimental techniques concerning the nature of this phenomenon, which is due in part to the limited number of measurement techniques. Our results using the NanoDSC shows promise as a tool for developing a more general understanding to this problem. Analysis of the glass transition obtained by NanoDSC of polystyrene, poly(2-vinyl pyridine) P2VP and poly(methyl methacrylate) PMMA shows (Figure 1) only modest thickness dependence. This particular NanoDSC experiments was done using a annealing/scanning technique described in Macromolecule [7].

The NanoDSC was also used to investigate the melting of Bi nanoparticles. The particles were formed by evaporating Bi onto a silicon nitride substrate. Upon deposition, bismuth self-assembles into truncated spherical particles. As the total amount of bismuth increases, the average size of the particles also increases. By systematically changing the “integrated” amount of Bi deposited (0.3, 0.6, and 2.0 nm) as shown in Figure 2, the size of the bismuth particle changes as can be seen in the TEM micrographs in Figure 2. The same samples as used for the NanoDSC measurements are also used for TEM via the specially designed sensor and fixture [9]. The companion heat capacity measurements of the nanoparticles, shown in Figure 2, indicate the subsequent decrease of the melting point for smaller size particles [8]. The nature of the size-dependence melting point decrease for bismuth is much different than for tin or indium as measured in previous experiments.

References:
Low Heat Capacity Substrates for Calorimetry Measurements

CNF Project # 522-94
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Figure 1: (A) Cross-sectional and planar views of a typical NanoDSC sensor with a polymer sample on it (not to scale). (B) Glass transition temperature of (circle) polystyrene, (diamond) high molecular weight polystyrene (square) poly-2-vinyl pyridine), and (triangle) poly-methyl methacrylate assigned using first-pulse curves of the annealing/scanning technique [Macromolecule, 37, 4607 (2004)].

Figure 2: (a-c) TEMs of various amounts of bismuth deposited on the Si-N side of the NanoDSC. Nominal equivalent thickness values are shown. As the total amount of Bi is increases the average size of the particles also increases. The bottom graph shows the corresponding heat capacity \( C_p \) data from these films and shows the decrease in melting point for smaller particles—size-dependent melting point depression [J. of Appl. Phys. 97, 34304 (2005)].
Ultrathin Silicon Nitride Membranes for use as a STEM Substrate

CNF Project # 877-00
Principal Investigator: Professor John Silcox

Abstract:
An ultrathin silicon nitride membrane with estimated thickness of 3 nm was produced for use as a sample substrate in a scanning transmission electron microscope (STEM).

Summary:
Silicon nitride membranes are routinely produced using standard procedures, and are available commercially for TEM use with membrane thicknesses reaching 20 nm. However, for the purposes of high-resolution imaging and electron energy loss spectroscopy (EELS) on the tiniest of nanoparticles using STEM, even such thin membranes can swamp the signal from the nanoparticle of interest. The goal of our project was, therefore, to produce silicon nitride membranes with thicknesses of 10 nm or less for use in Cornell’s STEM.

Silicon nitride was chosen as a substrate because, unlike ultrathin carbon substrates, silicon nitride has a bandgap of about 5 eV and can therefore hopefully provide a low-signal area in the low-loss region of the EELS spectra.

Using standard procedures of low-pressure chemical vapor deposition of silicon-rich silicon nitride on <100> silicon wafers, photolithographic techniques, and anisotropic KOH etching, we successfully produced ultrathin silicon nitride membranes. Using the FilMetrics film measuring system located in CNF, the silicon nitride thin film was optically measured to be approximately 5 nm thick on the silicon wafer.

Using STEM imaging, we examined the membranes at high resolution and observed pinholes throughout the film. Despite the extreme thinness of the sample, the silicon nitride membranes show remarkable strength, suspending large particles 4 µm in diameter!

The thickness of the silicon nitride membrane was measured in the STEM using EELS zero-loss and low-loss spectra. Initial estimates using this technique show the membrane to be 3 nm, however at these extreme limits it is not clear that this technique is valid.

Further work is to be done on these membranes by varying the ratio of silicon and nitrogen in an attempt to lower the overall Z-value of the membrane.

Silicon nitride membranes of 5-3 nm were produced for use as a scanning transmission electron microscope (STEM) substrate.
Ultrathin Silicon Nitride Membranes for use as a STEM Substrate

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Figure 1, top left: Optical microscope image of silicon nitride membrane. Bright spots are most likely specks of silicon created by the etching process. The buckling of the membrane seen here disappears as the windows decrease in diameter.

Figure 2, bottom left: STEM annular dark field (ADF) image of the membrane. Dark areas are possible pinholes.

Figure 3, above: STEM ADF image of the membrane as a substrate for CdSe quantum dots.
Nanocalorimeter Fabrication for Implantation Defect Investigations

CNF Project # 1048-02
Principal Investigator & User: François Schiettekatte

Abstract:

Nanocalorimetry is used to measure the heat release during the annealing of low-energy ion implantation damage in silicon. Low-stress silicon nitride is deposited by LPCVD at CNF in order to fabricate thin-film nanocalorimeters. These consist of a membrane that supports a metal strip, which serves as heater and thermometer during calorimetry experiments. Amorphous and polycrystalline silicon (a-Si and poly-Si) is deposited on the other side of the membrane and implanted with low-energy ions (4-30 keV) at fluences from $10^{11}$ to $10^{15}$ ions/cm$^2$.

In both types of silicon, we observe a striking similarity in shape of the heat release over the wide range of fluxes, suggesting that each impacting ion produces a damage zone similar to the damage generated by high fluence implantation, releasing heat in a same way during annealing. Experiments were carried out at heating rates between 33 and 144 kK/s, showing that the heat release is characteristic of a series of processes continuously distributed in terms of activation energy.

We also observe that implants at a lower beam flux translate into smaller heat release for the same fluence. Shorter implantation times at higher fluxes leaves less time for dynamic annealing and higher impact rate may stabilize disordered zones that would have enough time to undergo dynamic annealing at lower fluxes.

Summary:

Nanocalorimetry is a technique developed by the group of Leslie H. Allen at the University of Illinois in collaboration with the CNF, and used successfully to measure the heat involved in a variety of phase change and chemical reactions occurring at the surface of materials [1]. It operates on the same principles as conventional differential scanning calorimetry (DSC) but the thin-film structure of the device provides a small addendum and allows fast heating rates (up to $10^6$ K/s), making possible the observation of thermal processes involving energy exchanges of the order of the nJ/K. Our devices consist of a low-stress Si$_x$N$_y$ membrane (180 nm, deposited at CNF) that supports a 0.5 mm wide, 7 mm long Pt heating strip. The current flowing through and the voltage drop along the strip are measured and provide power and resistance measurements, the latter being used to measure the temperature of the strip as a function of time. For our investigations, a 140 nm a-Si film is deposited in correspondence with the Pt strip, and can be recrystallized at 900°C for 100 s in order to form poly-Si [2].

In this research project, we use nanocalorimetry to investigate, from the thermal point of view, the kinetics of damage annealing following low-energy ion implantation in a-Si and poly-Si. We found that the heat released has the same profile over the fluence range examined ($10^{11}$ to $10^{15}$ ions/cm$^2$), featuring no peaks but rather a smooth, continuous shape. This result suggests that each impacting ion produces a high-damage zone similar to the damage generated by high-fluence implantation. Such heat release is thus interpreted as the result of highly damaged zones that undergo annealing by small recrystallisation and relaxation steps, each step featuring a wide range of activation energies [3]. As it depends of the details of the damage structure of each ion, the annealing kinetics in silicon is thus independent of ion fluence and implantation energy (4-30 keV).

Experiments were carried out at heating rates between 33 and 144 kK/s. The shape of the heat release and its behaviour with increasing heating rate is characteristic of a series of processes continuously distributed in terms of activation energy [4]. Ion beam flux was also investigated and it was shown that damage annealing releases more heat for implantations carried out at higher flux, suggesting that damage undergoes more dynamics annealing at comparatively lower flux, simply because the implantation time is longer. Another interpretation is that more frequent impacts stabilize structure by producing displacements around a previously damaged region before it has time to dynamically anneal.

References:


Nanocalorimeter Fabrication for Implantation Defect Investigations

CNF Project # 1048-02
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Figure 1, above: Thin film calorimeters fabricated using LPCVD low-stress nitride deposited at CNF.

Figure 2, top right: a) Heat release after 30 keV Si implantation in poly-Si for a wide range of fluences. b) The normalized signal shows that the heat release is the same at all fluence, indicating that the underlying processes are similar.

Figure 3, bottom right: Heat released by poly-Si implanted with 30 keV Si at 0.1 Si/nm² for different heating rates. The heat release is characteristic of a wide distribution of activation energies.
Improving Mechanical Reliability of Si Nanobeams with Self Assembled Monolayers

CNF Project # 1154-03
Principal Investigator: Alan T. Zehnder

Abstract:
The fracture durability of silicon nano-beams in air was improved considerably by methyl surface termination. 210-nm thick, doubly clamped beams with functionalized surfaces were tested after exposure to air over a period of 23 days. Experiments showed that the native oxide growth reduced the strength of the beams with H terminated surfaces from 16.2 GPa to 11.2 GPa. Coating the sample surfaces with methyl monolayers prevented oxidation and maintained the strength throughout the test period under same environmental conditions.

Summary:
Due to their small sizes and use of materials with very low defect densities, materials used in the nanoscale have the potential to sustain very high stresses. For microelectromechanical system (MEMS) applications, as important as the high initial strength, is the prevention of aging of the structure throughout its service life. Si devices operating in air are expected to have very high durability under mechanical loading as Si is not susceptible to stress corrosion cracking. However, the native oxide layer (amorphous SiO$_2$) may enhance fracture initiation and cause catastrophic failure [1]. How does air exposure influence the fracture reliability of single crystal Si under static loading? And how can the service life of Si structures in air be improved? Our study shows that effective protection of the surfaces is essential for the maintenance of the mechanical strength of nanostructures.

To characterize the effects of air exposure on the fracture reliability of nanostructures, 210-nm-thick, 500-nm-wide, 12-µm-long doubly clamped suspended beams with H and CH$_3$ terminated surfaces were fabricated from Si (111) wafers using previously described procedures [2,3]. After their fabrication, samples with different surface terminations were exposed to office air and tested at the 3rd, 13th and 23rd days with an AFM [4].

The Weibull strength, $\sigma_0$, of the H-terminated beams decreased steadily from 16.2 GPa to 11.2 GPa with increasing air exposure time, whereas the strength of the CH$_3$ terminated samples remained at 18 GPa over the test period of 23 days.

It is known that H-terminated surfaces show only a temporary protection against oxidation. An approximate 7-day air exposure results in an oxide thickness of 1.5 nm for H-terminated Si (111) [5]. The native SiO$_2$ has a lower fracture resistance and is prone to undergo moisture assisted cracking under applied stress. With increasing oxide thickness, the load that is necessary to initiate the crack, and hence the observed fracture strength, decreases. It should also be noted that the native oxide, unlike thermally grown oxide, does not necessarily have uniform properties. Its thickness and quality change randomly on the surface. We hypothesize that the inhomogeneous oxidation of the surface results in randomly distributed, local residual stresses, which, together with the increase in surface roughness may enhance fracture initiation, hence reducing the strength of the tested beams.

Our results show that methyl surface coating effectively protected the surfaces for up to 23 days by preventing oxidation and allowed fracture strengths to be maintained.

References:
Improving Mechanical Reliability of Si Nanobeams with Self Assembled Monolayers

CNF Project # 1154-03
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• Surface protection plays a crucial role in maintaining the mechanical reliability of Si nanobeams.

Figure 1, top left: Weibull fracture probability plot of beams with H terminated surfaces. Inset: a) A test beam before and b) after the experiment.
Figure 2, bottom left: Weibull fracture probability plot of beams with CH$_3$ terminated surfaces.
Figure 3, above: Change in Weibull fracture strength of beams with H and CH$_3$ terminated surfaces with increasing air exposure.
Nanoporous Gold Thin Films

CNF Project # 1163-03
Principal Investigator: Christopher Umbach

Abstract:
Nanoporous gold (NPG) can be fabricated as a thin film by the sputtering of Ag-Au onto suitable substrates followed by a wet chemical dealloying treatment. During dealloying, removal of the silver and redistribution of gold results in a nanoporous network with openings on the order of 10 nm. Metallic buffer layers allow the fabrication of crack-free films that remain adhered after dealloying. The thin-film NPG shows the same morphology after dealloying as that of a NPG produced from a 200 µm thick membrane sheet of the alloy. The pore structure of both the thin film and the bulk membrane can be coarsened through annealing.

Experimental Details:
Nanoporous gold has potential for filtration of nano-objects and use in high surface area detectors and ultracapacitors. Thin-film implementation of NPG allows the use of this material in devices at lower cost. We have fabricated thin film NPG on conventional substrates. Both glass and oxidized silicon were used as substrates. Glass substrates were first cleaned with distilled water and then methanol in an ultrasonic bath for several minutes before being plasma cleaned for 10 minutes. In CNF, Si wafers were MOS cleaned and then wet oxidized to a thickness of 100 nm. Chromium was evaporated as an adhesion layer, on top of which gold was evaporated as a buffer layer. The uniform metallic buffer layers were deposited in NBTC using a CHA Mark50 evaporator. Ag-Au (70%-30%) alloy was used as a target in a Baltec sputter coater to deposit films with thicknesses ranging from 100 nm to 500 nm. Diluted nitric acid was used to dissolve the silver from the Ag-Au alloy. Samples were annealed in either an oxygen atmosphere or in a vacuum. The annealing took place at 200°C and lasted four hours. Samples were imaged with both atomic force microscopy in NBTC and with high resolution Zeiss Ultra SEM in CNF.

Results:
The nanoporous thin films exhibit a morphology similar to that of the bulk membrane both in pore size (generally between 20 and 30 nm) and degree of interconnectedness. The films deadhered upon dealloying when the Au/Ag alloy was deposited on only a chromium adhesion layer. Best adhesion was observed with the gold buffer layer. The samples dealloyed for 12 hours appear to be less pore-dense than when dealloyed for several minutes. The pore openings can be increased to several hundreds nanometer by annealing.

Summary:
NPG films have been fabricated on glass and Si substrates. The pore size and pore density of the films is similar to that observed for NPG fabricated from bulk alloy material.

References
Nanoporous Gold Thin Films

CNF Project # II63-03
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• Films deposited by sputtering: 70/30 at % Ag/Au alloy target.
• Dealloying in diluted nitric acid produces nanoporous gold.
• Initial pore size ~ 30 nm.
• Similar to dealloyed bulk membrane sheet.
• Pore size increases with annealing.

Figure 1: (a) 200 µm bulk membrane sheet dealloyed 12 hours. (b) 200 nm thin film dealloyed 10 minutes.

Figure 2: Average pore size with increasing time of annealing at 200°C for bulk membrane and for thin film.
Self-Assembly of Non-Spherical Colloids

CNF Project # 1177-03
Principal Investigator: Abraham D. Stroock

Abstract:
There exists an outstanding need for methods with which to form complex, three-dimensional structure on the colloidal scale (10 nm-10 µm). Such methods would be valuable for the development of photonics, high density memory and electronics, and micromechanical devices. An attractive approach to this challenge is to exploit the concepts of chemical thermodynamics to form structure from colloidal building blocks. This approach, based on self assembly, requires the development of a diversity of building blocks (elements), selective and directional interactions (bonds), and methods of processing (reactions). In this project, we are developing a self assembling colloidal system based on direct lithographic fabrication of particles and tailored electrostatic, van der Waals, and depletion interactions.

Summary:
We have developed a procedure by which to form right-cylindrical particles directly from a negative photoresist, SU-8 2002 (Microchem). The key aspects of the process are: 1) spin casting a sacrificial layer (Omnicoat) on a 4-in. silicon wafer; this layer is dissolved in order to release the particles. 2) Spin casting a layer of SU-8; this step defines the height, \( h [\mu m] \) of the particles that will be formed. 3) Exposure of layer of SU-8 through a photomask (GCA Autostep 200 DSW i-line Wafer Stepper) and development; these steps define the diameter, \( d [\mu m] \), of the particles. 4) Release via dissolution of the sacrificial layer, washing via repeated centrifugation, and stabilization in aqueous solution with a non-ionic surfactant (Tergitol, NP-40). This route to the formation of particles generates \( \sim 10^9 \) colloidal particles on a 4-in. wafer. We have formed particles with thicknesses in the range, \( 0.2 < h < 3 \mu m \), and diameters in the range, \( 0.9 < d < 8 \mu m \). The nominal resolution of the Autostep 200 is 0.5 µm. We have also generated non-circular, right parallelepipeds in SU-8.

Analysis of scanning electron micrographs (SEM) of lithographically-defined particles in SU-8 indicates that the distributions of size and shape are narrow within a single wafer (Figure S1): \( \Delta d = \pm 5\% \) and \( \Delta h = \pm 4\% \) for 1:1 and \( \Delta d = \pm 5\% \) and \( \Delta h = \pm 4\% \) for 1:3. SU-8 is a complex epoxy with a density after curing of \( \rho = 1.2 \text{ g/cm}^3 \). We note the roughness of the surface of the particles: the sides are significantly rougher than the top and bottom. This contrast in the roughness is likely to play a role in defining the interactions between particles.

Here, we present results for right cylindrical particles of aspect ratio 1:1 (\( h = 1.2 \mu m, d = 1.2 \mu m \)) and 1:3 (\( h = 0.4 \mu m, d = 1.2 \mu m \)). These right cylindrical particles allow us to explore the role of particle shape in dictating colloidal interactions. The three principal types of interactions that cylinders can undergo: flat-to-flat, flat-to-curved, or curved-to-curved. We expect that the attractive interactions, due to both van der Waals and depletion interactions, will be stronger between surfaces that can form closer contact with one another. Thus, the flat-to-flat conformation should be most thermodynamically favorable, followed by flat-to-curved, and, finally, by curved-to-curved. State diagrams of the structures formed in dispersions of these particles illustrate this shape-selectivity: as the electrostatic repulsion between the particles is diminished with rising ionic strength and the depletion interaction is increased with rising concentration of a non-adsorbing polymer, the particles pass through a columnar state in which aggregation occurs with strong selectivity for end-to-end assembly. These results demonstrate the rational design of a colloidal system that exhibits self-assembly of ordered, highly anisotropic structures.
Self-Assembly of Non-Spherical Colloids

CNF Project # 1177-03
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Users: Stephane Badaire, Cecile Cottin-Bizonne, Joseph Woody

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Goals:
1) Investigate the role of shape in defining the interaction between colloidal particles and
2) develop a set of tools with which to self assemble structures on the 100 nm to 100 µm scale.

Figure 1: Fabrication of colloids. (A) Schematic diagram of formation of cylindrical particles in a photocurable epoxy (SU-8) via projection photolithography (Autostep 200 - 10x stepper). (B) Scanning electron micrograph of particles formed by the process in (A). Scale bar = 1 µm.

Figure 2: Selective interactions tuned with shape, electrostatics, and depletion. (A) Orientations of interaction of cylindrical particles. (B) Diagrams indicating structures observed in dispersions of cylindrical particles of aspect ratio 1:1 (h = 1.2 µm; d = 1.2 µm in A) at various ionic strengths, I [mM] and volume fractions of dextrane, φd [v/v %]. (C) Optical micrographs of columnar state for 1:1 particle with I = 15 mM and φd = 0.5%. Scale bar indicates 10 µm.
Mimicry of Biological Adhesion Through Fabrication of Fibrillar Surfaces

CNF Project # I225-04
Principal Investigator: Anand Jagota

Abstract:
Geckos and other lizards as well as many species of insects utilize fibrillar contact surfaces to enhance their ability to adhere to a wide variety of natural surfaces. This work seeks both to understand and mimic the distinctive biological geometry and its superior non-covalent adhesion performance.

Summary:
We have shown theoretically that a fibrillar surface in contact with a substrate can possess both larger adhesion force and larger fracture energy than a corresponding flat interface of the same materials [1,2]. To verify this theory and mimic the benefits observed in biological systems, we constructed microscopic fibrillar arrays using the capabilities available at CNF.

Fibrils were constructed with diameter equal to 10 µm, nearest neighbor spacing between 20 and 120 µm and length between 10 and 100 µm. To make these fibrillar arrays, standard photolithography and deep reactive ion etching was used to produce holes in Si with the desired cross-sections and depths. This Si master surface was then used to mold poly(dimethylsiloxane) (PDMS), which was cured and removed from the master to give fibrils of the same shape and size as the holes in the Si surface. To enable release of the PDMS structures from the master, molecular vapor deposition of (1H,1H,2H,2H-perfluorooctyl)trichlorosilane was used to form a hydrophobic self assembled monolayer on the Si.

We showed in previous experimental work [1] that the fibrillar arrays alone are not sufficient to increase adhesion over the flat control value, due to the large loss of contact area accompanying fibrillation. Hence, a thin film was adjoined to the terminal ends of fibrils in this set of samples. This film was made of PDMS approximately 4 µm thick, formed by spinning PDMS onto a hydrophobic SAM coated Si wafer. While the film was still liquid, the fibrillar arrays were placed on the film. The PDMS liquid wetted the PDMS fibrils and was cured in place to form the terminal film. Later, the sample was removed mechanically from the substrate.

The addition of the terminal film is instrumental in the functioning of the fibrillar adhesion arrays in several ways. First, it increases the available contact area to the maximum possible value, equal to that of the flat control. At the same time, the fibril and thin film hybrid is much more flexible than the bulk flat control sample, allowing contact to form more easily with the adherend. It also turns out that the combination of flexibility and contact allowed by the thin film is responsible for increasing adhesion because of unstable crack propagation and contact pinning [3]. Finally, the film maintains the separation and uprightness of the pillars because there is an energy penalty associated with stretching the film that prevents neighboring fibrils from adhering to each other, a problem with free standing fibrillar arrays.

Results for the adhesion of the film terminated fibrillar arrays are positive. One experiment involved peeling the fibrillar sample from a substrate. The energy per unit area associated with peeling the fibrillar samples was found always to be larger than that for corresponding flat controls, by a factor of 2 to 9. Another experiment involving indentation with a spherical indenter showed that the fibrillar pull off force was also larger than the flat control values, by a factor of 1.5 to 3. The variation depends on the precise geometry of the fibrillar array and film. Although a rigorous study is not yet complete, preliminary experiments indicate that adhesion enhancement increases with increasing fibril spacing and decreasing film thickness and fibril diameter.

References:
Mimicry of Biological Adhesion Through Fabrication of Fibrillar Surfaces

CNF Project #1225-04
Principal Investigator: Anand Jagota
Users: Nicholas J. Glassmaker, Shilpi Vajpayee

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- A fibrillar array with terminal film mimics the contact and adhesion enhancement achieved by geckos and insects. (Figures 1 and 2)
- Synthetic fibrillar samples constructed by photolithography, dry etch, and molding.
- Fibrillar samples achieved greater adhesion force than flat controls in indentation experiments. (Figure 3).

Figure 1, top left: Fibrillar surface, lizard. (Anolis carolinensis.)

Figure 2, bottom left: Synthetic poly(dimethylsiloxane) fibrillar surface with terminal film.

Figure 3, above: Fibrillar adhesion force, normalized by flat control values.
Development of Quantum Dot Encoded Polystyrene Beads for Use in an Ultra-Miniaturized Microarray Platform

CNF Project # 1235-04
Principal Investigators: Alexander Couzis, Charles Maldarelli, Lane Gilchrist

Abstract:
An ultra-miniaturized micro-array platform, displaying probe molecules, is conceptualized for high-throughput, multiplexed screening applications. The probes are incorporated in a unilamellar phospholipid bilayer supported on polystyrene (PS) beads of ~1 µm diameter. This whole assembly is called a lipobead. The lipobeads are inserted in wells of corresponding size, etched in a square grid pattern on silicon wafers using photolithography and functionalized with self assembling monolayers (SAMs) with pendant groups designed to bind a single bead to the inside of each well. The area on the substrate surrounding the wells is chemically functionalized with a polyethylene glycol (PEG) terminated SAM to resist non-specific adsorption in screening assays. An encoding scheme based on the fluorescence of hydrophobically modified zinc sulfide (ZnS) capped cadmium sulfide (CdSe) core-shell semiconductor nanocrystals (quantum dots (QDs)) is used for identification of the receptors hosted by individual lipobeads. QDs with different emission wavelengths (colors) and encapsulation concentrations are used to define a code based on intensity (i) and color (c). The encapsulation is undertaken by copolymerizing the styrene and methacrylic acid with the QDs using a suspension polymerization procedure. The bar-coded PS beads with carboxyl termination are then mixed with lipid films incorporating the probes. The array is assembled by first preparing aliquots of beads, with each aliquot consisting of beads with the same QD barcode, mixing aliquots together and finally depositing the bead mixture onto the microwell grid surface. Confocal laser scanning microscope is used for detecting the bar-codes.

Summary:
This array of optically encoded beads is designed to be used as a protein or chemical microarray. Probe molecules are bound to the bead surfaces (with each probe identified with a QD bar code) and screened against targets present in a solution deposited as a microliter drop on the array surface. Binding of a target to a probe is detected usually by the luminescence of a fluorescent label on the target. By reading the code on the bead lit by this label, the identity of the probe molecule binding the target can be obtained. This design has several advantages over conventional protein and chemical arrays. The micron-scale of the beads and the grid allows a registry density of $10^5$, which is orders of magnitude larger than the density of conventional arrays consisting of dried spots of probe molecules with each spot of the order of approximately 100 µm. The encoding capacity of the QDs ($i^c$) allows for the bar coding of this large number of registries. In addition, by coating the beads with bilayers and sequestering membrane receptors in the bilayers, this platform can be used for the display of difficult to present membrane receptors which require a lipid environment to retain their biological binding ability.

As a proof of concept, 1 µm diameter carboxyl-functionalized fluorescently tagged PS particles (excitation maxima, 529 nm; emission maxima, 546 nm; obtained from Polysciences, Inc.) were arrayed on the 1.2 µm diameter microwell grid. A flat block of polydimethylsiloxane (PDMS) impregnated with PEG-terminated silane was used to put down a PEG-terminal background phase using contact printing. 3-aminopropyltrimethoxysilane (APS) was used to backfill the ‘bare’ wells. This grid was exposed to 0.0025% (wt) solution of particles for 24 hrs and then rinsed with DI water and imaged under the confocal laser scanning microscope. The negatively charged particles are electrostatically coordinated with the positive amine termination of the wells. The passivating PEG functionality surrounding the wells allowed for the easy removal of the non-coordinating particles.

Reference:
Development of Quantum Dot Encoded Polystyrene Beads for Use in an Ultra-Miniaturized Microarray Platform

CNF Project # I235-04
Principal Investigators: Alexander Couzis¹, Charles Maldarelli¹², Lane Gilchrist¹
Users: Shyam V. Vaidya¹, Nikhil D. Kalyankar¹

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Figure 1

Figure 2

Figure 1, top left: Schematic of conceptualized micro-array platform displaying targets interacting with the probe molecules in the lipobead.

Figure 2, bottom left: Microwell surfaces fabricated using photolithography: diameter of wells = 1.2 µm, depth of wells = 0.55 µm, pitch = 3 µm.

Figure 3, above: (a) Confocal laser scanning microscopy image of fluorescing PS particles electrostatically arrayed on functionalized grid surface, (b) y-section image along the line shown in (a).
High-Throughput Determination of Mechanical Properties using Microcantilever Arrays

CNF Project # 1236-04
Principal Investigator: R. Bruce van Dover

Abstract:
We are developing a platform for measuring the composition-dependent mechanical properties of materials using an array of microcantilevers. The goal is to be able to investigate the properties of nearly all compositions in a ternary phase diagram with 1 atomic percent (at.%) resolution in a single experiment, and to use this capability to determine trends and identify unusual and/or useful materials in a wide range of ternary systems [1]. Our approach is to prepare a large array of prefabricated cantilevers on a single wafer, deposit a composition-spread thin film on the array, and interrogate each cantilever as a function of some probe stimulus (temperature change, magnetic field, etc.) and thereby infer the composition-property relationship. Our initial experiments are aimed at measuring magnetostrictive materials, for example in the Fe-Ni-Al ternary system. The composition-spread films are deposited using three spatially-separated sputter guns, yielding a typical composition gradient on the order of 1 at.% per mm. In order to determine the properties with ~ 1 at.% resolution, we therefore require microcantilevers located on ~ 1 mm centers. This approach eliminates the run-to-run variations that can confound one-off experiments. With an automated measurement system that is capable of characterizing in one day the response of a 3,000-cantilever array representing an entire ternary phase diagram, this technique enables investigation of magnetostriction in thin films with unprecedented composition resolution and speed. Our “combinatorial” platform will also enable studies of other mechanical properties of advanced materials such as conventional and ferromagnetic shape-memory alloys.

Summary:
All of our device preparation is done at the Cornell NanoScale Science & Technology Facility (CNF). We choose Si$_3$N$_4$ as cantilever material because it is straightforward to deposit and requires only a single lithographic step. We use the nitride tube furnace to deposit ~ 1 µm of low-stress LPCVD Si$_3$N$_4$ on a <100> silicon wafer. Patterns are transferred by standard photolithography using the GCA 5X stepper. After exposure, MIF 300 base developer is used to develop the patterns and PlasmaTherm72 reactive-ion etcher is used to etch the nitride. After stripping photo resist, KOH is used to wet etch the Si to undercut cantilevers—the Si <111> surface acts as etch stop. A CO$_2$ critical-point dryer is used to dry and release the cantilevers to avoid sticking. With our current design, cantilevers are designed to have dimensions of 500 µm x 50 µm and are spaced 1 mm apart in a square array. These dimensions ensure that each cantilever is small enough that the composition of the film on the cantilever is essentially constant, and that composition-dependent properties can be interrogated with a resolution of ~ 1 at.%. The composition-spread thin films are deposited in a custom-designed sputtering system in our lab.

At the center of our measurement design, the cantilever acts as a base substrate for a deposited thin film whose properties (for example, intrinsic stress, shape memory, or magnetostriction) are to be measured [2]. For magnetostriction measurements, the curvature of the deposited bilayer film-substrate cantilevers are measured as a function-applied magnetic field. The cantilever base has essentially no magnetic response, so the Stoney formula for bending of a cantilever under differential stress can be adapted to the present magnetostriction measurements to give:

$$\lambda = D \frac{E_s t_s^2}{E_f t_f^2} \frac{(1 + \nu_f)}{(1 + \nu_s)(1 - \nu_s)}$$

where $\lambda$ is the magnetostrictive response, $D$ is the vertical deflection at the end of the cantilever, $E_s$ is Young’s modulus of the cantilever, $t_s$ is the thickness of the substrate, $t_f$ is the thickness of the film, $l$ is the length of a cantilever and $\nu_f$ and $\nu_s$ are the values for Poisson’s ratio for the substrate and film [3], respectively. The deflection of the cantilever depends only on the differential strain between the film and cantilever base material. Thus this approach can be used for measurement of any source of differential strain, such as differential thermal expansion and, importantly, shape memory materials.

References:
High-Throughput Determination of Mechanical Properties using Microcantilever Arrays

CNF Project # 1236-04
Principal Investigator: R. Bruce van Dover
Users: Noble C. Woo, Bryan G. Ng
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Figure 1, top left: Fabrication process flow of a Si₃N₄ cantilever.

Figure 2, middle left: Cantilever bending measurement setup. Changes in cantilever curvature due to magnetostriction under an applied magnetic field will modify the optical path of the laser, which is detected by a position sensitive detector, analyzed by software, and reported in terms of the differential strain.

Figure 3, bottom left: (Left) Intrinsic stress in thin films of Ni-Fe-Al, as inferred from cantilever deflections as a function of position in a composition-spread sample. Labels indicate the approximate position of the elemental sources creating the composition spread. (Right) Photograph of the sample.
Scanning Electron Microscope and Focused-Ion Beam Analysis of Corrosion Sites on Lead-Tin Alloys

CNF Project # 1346-05
Principal Investigator: Catherine M. Oertel

Abstract:
Focused ion beam (FIB) was used to cut micron-scale cross-sections through corrosion crusts on acetic-acid corroded lead-tin alloys. The exposed surfaces were mapped chemically using SEM/EDX. The results of the mapping provide insight into the role of tin content in susceptibility of these alloys to organic acid attack.

Summary:
Lead-tin alloys are the most common materials used to construct organ pipes, both in instruments built today and in those remaining from past centuries. Corrosion of these pipes is widely observed, eventually leading to cracks and holes that rob the pipes of their ability to produce sound. Especially for irreplaceable historic instruments, this corrosion is of great concern, and research is needed to determine its causes and mechanisms.

For very lead-rich ( > 99% Pb) alloys, organic acids have been found to be a major cause of corrosion [1]. The acetic acid emanating from the wood of organ cases is likely to be a source of damage in lead-rich pipes. Our research has as its goal understanding how the susceptibility to acetic acid attack changes as a function of alloy composition. We carried out laboratory exposure experiments in which lead-tin alloy coupons were exposed to low, controlled concentrations of acetic acid vapor. Alloys with tin contents ranging from 1-10% were studied. We used grazing incidence angle x-ray diffraction to identify the bulk corrosion products that formed on the sample surfaces, but we needed more detailed analytical methods that would allow us to characterize the morphology of corrosion products and to resolve chemical information at corrosion sites.

Using the Zeiss Supra SEM at CNF, we obtained images of sample surfaces at magnifications ranging from 100x-4000x. The low-mag images revealed that the surfaces are not covered with uniform corrosion layers but that corrosion crusts with dimensions of 10-100 µm are interspersed among areas with thin oxide coverage. At high magnification, it was possible to see the individual 1-2 µm crystallites making up the thick crust areas.

Next, we used the FEI 611 FIB to cut cross sections of 10-20 µm through corrosion crusts. Compared with traditional sectioning and polishing, this is a gentler method of preparing cross-sections for SEM analysis. The gallium ion beam does not cause mechanical damage to the corrosion crust or the underlying bulk metal, and by following removal of significant material with a high beam current (2000 pA) with a polishing step at lower beam current (500-1000 pA), it was possible to minimize impregnation of the surface with gallium.

Each cross-section was cut at a 45° angle with respect to the surface normal, creating a surface that is horizontal when the sample itself is tilted at 45° in a microscope. In this orientation, SEM/EDX (using the Zeiss Supra) or SEM/WDS (using the JEOL microscope located in Snee Hall at Cornell) was used to map lead, tin, and oxygen content in the oxide crust and underlying metal. For each alloy, tin was segregated along the oxide-metal interface, allowing us to hypothesize that it has a barrier role in the corrosion process. Current work is being directed at using similar cross-sectional analysis to track evolution of this segregated layer with time and under atmospheres of varying humidity.

References:
Scanning Electron Microscope and Focused-Ion Beam Analysis of Corrosion Sites on Lead-Tin Alloys

CNF Project # 1346-05
Principal Investigator: Catherine M. Oertel
Users: Catherine M. Oertel*, Annika Niklasson**

Affiliation: Cornell Center for Materials Research, Cornell University
Primary Funding: NSF Discovery Corps Fellowship Program
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Figure 1, top left: Lead-tin alloys were exposed to low concentrations of acetic acid, simulating the conditions that lead to deterioration of lead-tin alloy organ pipes. This micrograph shows a surface with discrete corrosion crusts separated by areas of thin oxide coating.

Figure 2, bottom left: A FIB cross-section cut at 45° to the surface normal can be studied with SEM/EDX.

Figure 3, above: An image of the cross-section shows the oxide layer and bulk metal, containing tin inclusions.

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Pathways to Thin Film Ceramic Porous Membranes for Fuel Cell Applications

CNF Project # 1356-05
Principal Investigator: Ulrich Wiesner

Introduction:
Proton exchange membrane (PEM) fuel cell technology is considered to be a promising alternative for future energy needs due to a high energy conversion efficiency and lower environmental impact. The fuel cell basically contains an anode and a cathode separated by a PEM. The PEM has two major functions: it serves as a proton conductor and as an electronically insulating mechanical separator between the two electrodes. Current technology uses a PEM that is a composite of highly porous Teflon® backfilled with a perfluorosulfonic acid-containing polymer solution commercially known as Nafion®. The Nafion® polymer is the proton conductor whereas the Teflon® provides structural integrity. A major failure mechanism of the fuel cell is due to the expansion/shrinking of the membrane during temperature and hydration cycles. This expansion/shrinking behavior, especially in the plane of the film, may lead to cracking of the membrane which may cause decreased cell performance or complete failure. Those limitations may be overcome by replacing the Teflon® support by a ceramic material like silicon carbonitride (SiCN). Since the ceramic material has a significantly lower expansion coefficient compared to Teflon®, the expansion of a ceramic-nafion composite membrane in the plane of the film should be significantly reduced. Expansion may still occur by increasing the thickness of the film (the z-direction), but this can be managed easier due to cell design. The lower expansion of the membrane in the plane of the film (x-y direction) should increase the resistance of the membrane to failure.

The ceramic we chose to work with is a polyureamethylvinylsilazane (PUMVS), which is a so-called polymer derived ceramic [1]. As the name suggests, polymer derived ceramics start out as a polymer, which can be easily shaped into complex structures. Heat treatment transforms the polymeric precursors into ceramic materials, while retaining the original (complex) shape. Thus these materials have a polymer-derived structure and ceramic-like properties [2]. Here we show the use of polymer derived ceramics in combination with a stamping technique to develop porous ceramic membranes to replace the Teflon® support currently used in PEM fuel cell technology.

Results:
The synthesis of the ceramic porous membranes consisted of several steps. First a direct laser pattern generator was used to generate a 5 by 5 cm mask consisting of a hexagonal array of pillars. The diameter of one pillar was 25 µm and the center to center distance between pillars was 33 µm, to ensure 60-80% porosity of the final membrane. The stamp was made by photolithographic patterning of SU-8 by UV exposure through the mask using the HTG contact aligner, followed by baking and development of the non-exposed SU-8.

The stamp was clamped onto a silicon wafer coated with poly(acrylic acid). This assembly was subsequently dipped into a solution of the liquid PUMVS and a radical initiator. Driven by capillary force, the solution filled the interstitial spaces between the stamp and the coated wafer. Heat treatment of the assembly at 130°C in a vacuum oven crosslinked the PUMVS. The film was released by putting the assembly on a water surface and dissolving the poly(acrylic acid). The resulting film was robust enough to pick up with tweezers without disintegrating. Heat treatment to 50°C transformed the membrane into a porous ceramic membrane without losing its integrity.

References:
Pathways to Thin Film Ceramic Porous Membranes for Fuel Cell Applications

CNF Project # 1356-05
Principal Investigator: Ulrich Wiesner
User: Marleen Kamperman
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Primary Funding: General Motors
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Figure 1, top: Stamp consisting of a hexagonal array of SU-8 cylinders.

Figure 2, middle: Stamp and poly(acrylic acid) coated silicon wafer are clamped together. A mixture of polyurea methylvinylsilazane and thermal initiator is drawn into the interstitial spaces by capillary force. The polysilazane is crosslinked at 130°C. The stamp is removed and the porous polysilazane film is lifted off on water.

Figure 3, bottom: Light microscope image of the resulting porous polyureamethylvinylsilazane film.
Nanofabrication of Multifunctional Nanoscale Materials within Nanoporous Materials and on 2-D Substrates

CNF Project # 1448-06
Principal Investigator: Tewodros Asefa

Abstract:
Our research group is interested in developing novel nanostructured materials possessing multifunctional groups; these materials are created by combining “bottom-up” and “top-down” synthetic approaches such as electrodeposition, electroless deposition, chemical vapor deposition, self-assembly, sol-gel processing, wet-chemical synthesis, and reactive ion etching. The two or more functional groups or structures introduced into these materials have resulted in the material possessing two or more properties which allow them to perform either multiple applications or to increase the efficiency of the optical response and the magnetic and catalytic activities of the materials. By virtue of their multifunctional groups as well as structures at the nanoscale, these materials will find future applications in photovoltaics, nanoelectronics, and nanophotonics devices and for catalysis and biomedical applications.

Summary:
The design, synthesis and self-assembly of nanostructured materials are important steps leading to the development of novel miniaturized nanoscale devices for optical, electronics, photonics, sensing, biological or medical applications. To realize the tremendous potential of nanomaterials for diverse applications, we use various “bottom-up” approaches of wet-chemical synthesis and molecular self-assembly combined with “top-down” approaches of engineering nanomaterials to create novel nanoscale materials having multiple functional groups with well-defined nanoscale structures.

In one approach, we prepare nanoporous alumina substrates (0.2 µm diameter and 10 µm width) via electrochemical anodization of aluminum thin films [1] and we use the resulting nanoporous materials as hard-templates to produce silica and organosilica coated conductive metallic nanowires such as copper, silver and gold via electrodeposition.

To perform the electrodeposition in the nanochannels of these materials, we first deposit thin conductive layers of metals on one side of the substrate either via sputtering or thermal evaporation. We have successfully used aluminum sputtered and silver thermal evaporated nanoporous alumina substrates for our electrochemical deposition experiments. Results to date indicate that the Ag thermal evaporated substrates work better for copper electrodeposition inside the nanochannels of the alumina forming well-defined nanowire structures. We speculate this success is because the silver thermal deposition on the nanoporous alumina formed smooth conductive layers. By changing the deposition times and deposition potentials, we have been able to regulate the length (or aspect ratio) of the nanowires. By introducing silica layers over the alumina nanoporous channels, we were also able to change the structures of the nanowires. For instance, by depositing a silica (or organosilica) layer inside the nanochannel surface of the porous alumina followed by electrodeposition, we were able to create metal-silica (or metal-organosilica) core-shell nanowires. Upon wet-etching the alumina hard-template, we were able to collect free standing metal-silica (or metal-organosilica) core-shell nanowires. The silica or organosilica layer in these materials, which has low dielectric constant, provides an insulating layer to the metal and would be an important component when assembling these nanowires on solid devices for future nanoscale electronic components [1]. The nanowire materials we prepared before and after deposition are characterized by methods such as scanning electron microscopy, transmission electron microscopy, atomic force microscopy, UV-Vis-NIR spectroscopy and X-ray diffraction.

In other work, we prepare metal-thiolate precursors by reacting metal chlorides with alkanethiols and we spin-coat the resulting metal-thiolate precursors on noble metal nanopattared Si-wafers. By performing e-beam lithography on the metal-thiolates decorating the substrates, we form nanopatterns and write semiconductor metal-sulfide nanostructures on the substrates by using seeded mediated nanostructure formation. For instance, by depositing Zn-dodecanethiolate on gold nanoparticle containing Si-wafer substrate followed by e-beam writing, patterns of semiconducting ZnS nanoparticles or nanowires preferentially grow around the gold nanoclusters form. Electron beams are used to pattern structures of noble metals such as gold nanoparticles from gold-thiolate on solid substrates. We characterize the resulting substrates with UV-Vis-NIR, atomic force microscopy and scanning electron microscopy.

References:
Nanofabrication of Multifunctional Nanoscale Materials within Nanoporous Materials and on 2-D Substrates

CNF Project # 1448-06
Principal Investigator: Tewodros Asefa
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Figure 1, left: Synthetic scheme of nanotube and nanowire deposition within the nanochannel pores of porous alumina “hard-template”. The arrows indicate nanotubes and nanowires that can be deposited within the nanoporous alumina via electroless deposition or electrodeposition, respectively.

Figure 2, below: Copper nanowires electrodeposited inside Ag-sputtered nanoporous alumina channels. This side-view image shows the copper nanowires as well as empty channels of the alumina nanochannels that are not yet filed. By controlling the deposition times and electrodeposition potential, we can grow metallic nanowires of various lengths.