Investigation of Acid Diffusion During Laser Spike Annealing with Systematically Designed Photoacid Generators

CNF Project Number: 386-90
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Abstract:
The post-exposure bake in the lithographic process has a primary influence on resist performance as the time/temperature profile controls both the diffusion of photogenerated acids and the deprotection of the resist backbone. We utilize a laser (CO₂) based scanned heating system to achieve sub-millisecond heating durations with temperatures up to the thermal decomposition limit of the resist. This research is aimed at using synthetic techniques to vary the structure of the photoacid generator (PAG) in order to learn about the role of PAG size and structure on acid diffusion during sub-millisecond heating.

Summary of Research:
The requirement for smaller feature dimensions continues to drive lithography research forward. In order to meet the requirements of the ITRS roadmap, it is necessary to investigate not only resist materials, but every step of the lithography process as well. By optimizing processing steps, it may be possible to push materials past their current limit on state of the art lithography systems.

The post-exposure bake (PEB) step in the lithography process has the most effect on the shape and size of the patterns produced [1]. The heat catalyzes the deprotection or cross-linking of chemically amplified resists by mobilizing the PAG in the resist matrix. Some diffusion of acid is necessary to start the reaction, however, uncontrollable acid diffusion has been held accountable for limiting resolution and increasing line edge roughness (LER) of patterned resists [2,3]. Controlling acid diffusion by altering resist chemistry has been studied extensively with the creation of polymer-bound PAGs, where the PAG is chemically bonded to the resist chain, thereby limiting its mobility [4,5]. These resists have shown reduced LER, but at the expense of sensitivity [5].

Our research is associated with changing the method of the PEB to improve resist performance. Resists baked on a hotplate are heated to a modest temperature, in the range of 100°C to 150°C for seconds to minutes. By heating the wafer with the laser, the film is subject to a high rate of heating and cooling, in the sub-millisecond timeframe. We have shown that laser-post exposure bake (l-PEB) has resulted in improved LER, along with greater sensitivity, demonstrating the excellent performance capability of the laser [6].

We have synthesized a set of PAG molecules with differing anion sizes, shown in Figure 1. The anion structure has been systematically varied to investigate the effects of anion size on diffusion behavior. The acid diffusion length was measured using a bilayer technique that has been previously reported [7, 8]. The resist on the PDMS stamp was exposed using an ABM contact aligner with dose steps from 0-20 mJ/cm², and tested at a variety of bake temperatures with both the hotplate and laser. Figure 2 shows the acid diffusion length of the various photoacids as a function of bake temperature. The acid diffusion length is shortened with l-PEB treatment, even though those wafers were brought to a higher temperature than those tested on the hotplate.

Figure 1: Structures of PAG molecules.

Figure 2: Acid diffusion behavior of the PAGs with hotplate and l-PEB.
By reducing the timeframe of the past exposure bake, we can see a distinctive change in the diffusion characteristics of the PAGs. There is also a definite trend in diffusion length with varying the anion size. As the anion gets larger, the diffusion length decreases. The patterning properties of the PAGs were tested with a JEOL 9300 e-beam lithography system. Figure 3 shows patterns achieved with both hotplate and l-PEB. The l-PEB method is shown to reduce the high-frequency line edge roughness (LER) of the patterns, from 12 nm to 9 nm, calculated by SumMIT software. This study has helped us identify PAGs for use with our new l-PEB system, with optimal diffusion behavior and promising lithographic properties.

References:
Room-Temperature Nanoimprint Process for Patterning Biomolecules

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Abstract:
Fluorinated solvents and photoresists have been found to be non-damaging to biomolecules such as proteins and DNA. We have developed a novel room-temperature nanoimprint patterning process using these materials. This process can be used at room temperature because it relies on controlling adhesion forces rather than polymer flow. Clean, reproducible features from 100 µm to 1 µm have been imprinted. This process has other advantages including not requiring a descum etch after imprint and also being capable of patterning large-area features. Finally, we have demonstrated the use of the patterns formed to pattern proteins via a lift-off step.

Summary of Research:
Conventional nanoimprint lithography (NIL) is incompatible with patterning biomolecules for two reasons. First, they are solution processed in harsh organic solvents, such as acetone, which damage biomolecules. Second, conventional nanoimprint relies on heating the imprint resist above its glass transition temperature ($T_g$) or melting temperature such that it can flow to take the form of a template mold. But, biomolecules are damaged if heated above 40°C, which is below the $T_g$ of most resists.

We have developed a novel nanoimprint process to address both these issues and successfully pattern proteins by nanoimprint lithography. To avoid using harsh organic solvents a fluorinated polymer, poly (1H,1H,2H,2H-decafluoromethacrylate), is used for the nanoimprint resist. Highly fluorinated materials are soluble in fluorous solvents such as hydrofluorooethers. The Ober group has published previously on the use of Orthogonal Processing for patterning of organic electronic materials [1, 2]. These materials have recently been shown to be non-damaging to biomolecules [3].

To avoid heating the resist during imprint we spun-coat a thin 200 nm-thick layer of the fluoropolymer, then pressed a rigid quartz template into this layer under 300 psi using the Nanonex 2500 tool. Although the resist doesn’t flow during this step, some areas of the resist are compressed while others aren’t. This sets up shear forces at the edge of features causing micro-cracks through the resist. Then when the pressure is removed and the template lifted off, the resist that was compressed is adhered to the template and removed with it. Figures 1 and 2 show demonstration patterns. For the resist to be successfully removed the adhesion between the resist and the template must be greater than the adhesion between the resist and the silicon substrate, as illustrated.
in Figure 3. These adhesion forces can be tuned by using surface treatments such as molecular vapor deposition of self-assembled monolayers, APTMS treatment, oxygen plasma cleaning or Piranha cleaning.

If the adhesion between the resist and substrate is sufficiently weak, it will be removed cleanly, so no etch step is required to remove any remaining ‘scum’ layer. Also, since the imprint process does not rely on the flow of polymer, the size of features patterned is not limited by the polymer flow distance. Large features can also be patterned right next to small features, and variation of fill factor across the wafer is not an issue.

To demonstrate the utility of this nanoimprint process, patterns in the resist were transferred into protein patterns by first treating the exposed silicon with APTMS to present an -NH group on the surface for the protein to bind to. Proteins were then put down from an aqueous solution. This was followed by fluorescent label that binds to the protein in order that the patterns can be imaged. The final step was to lift off the remaining parts of the resist in hydrofluoroethers, leaving well-formed protein patterns. The whole of this process can be repeated with a different protein to achieve patterns of more than one protein on the same substrate as illustrated in Figure 4.

References:
Development of an Organic-Inorganic Hybrid Nanoparticle Photoresist for Next-Generation Lithography

CNF Project Number: 386-90

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Abstract:

We have developed a transparent, high refractive index inorganic photoresist with significantly higher etch resistance than even the most robust polymeric resist. As patterned feature sizes continue to decrease, film thickness must be reduced in order to prevent pattern collapse. Normally thinner films prevent sufficient pattern transfer during the etch process, creating the need for a hardmask, thus increasing production cost. Compared to PHOST, we have shown over six times better etch resistance. Organic ligands have been attached to a zirconium oxide (ZrO$_2$) nanoparticle core to create an imageable photoresist. This resist has shown superior resolution with e-beam lithography, producing 30 nm features.

Summary of Research:

The semiconductor industry is currently patterning at the 45 nm node with 193 nm immersion lithography (193i). 193i has extended the lifetime of 193 nm exposure tools by introducing an immersion fluid in the gap between the resist and the lens of the tool [1]. This will expand the depth of focus, as well as increase the numerical aperture (NA), which will increase resolution beyond what was possible with dry lithography. Water has had success as an immersion fluid, enabling pattern dimensions of 45 nm with an NA of 1.35. Other high index fluids are currently in the development stage that can produce 30 nm feature sizes and below with an NA of at least 1.50 [2]. Next generation techniques such as EUV lithography are currently under investigation to push resolution limits to sub-30 nm and beyond. Regardless of the exposure tools that will be used, new resist platforms need to be developed to address current patterning issues as well as those that will arise with new technologies.

As pattern sizes reach the sub-30 nm range, it is necessary to use thinner films to prevent pattern collapse from high aspect ratios. An aspect ratio of 2:1 would require films in the 40-50 nm range. However, resist films are usually comprised of organic materials and cannot sufficiently resist the etch process as a thinner film [3]. Therefore, extremely high etch resistant structures must be studied and developed to allow pattern transfer to the underlying substrate. This study examines hafnium oxide based nanoparticles as a next generation photoresist material. This material provides benefits beyond the excellent etch resistance of a metal oxide. Metal oxides are extremely thermally stable, and because ZrO$_2$ cannot oxidize, it is chemically stable as well. It is possible to control the size of the nanoparticles through synthetic techniques [4], allowing the creation of small particles with a narrow size distribution, thereby increasing homogeneity of the film. We have previously studied hafnium oxide as a core for nanoparticle photoresists, which has shown excellent sensitivity and resolution with EUV patterning, as well as unprecedented etch resistance compared to state of the art resists [5]. ZrO$_2$ has been shown to be low absorbing at both 193 nm and EUV wavelengths (13.5 nm) [6]. ZrO$_2$ nanoparticles with methacrylic acid (MAA) ligands were synthesized and patterned using e-beam lithography and photolithography. ZrO$_2$ is used as a core to increase the etch-resistance of the resist. Besides the nanoparticles, a photoactive compound was added into the resist formulation to generate a photochemical reaction upon exposure and change the solubility of the resist. An organic developer is used to develop the resist and we were able to achieve negative-tone patterns. We have patterned the resist using an ABM contact aligner at 254 nm and using the JEOL 9300 e-beam lithography system. High-resolution negative-tone patterns have been achieved (Figure 1) using e-beam radiation with feature size as small as 30 nm.

One of the most important aspects of this photoresist is etch resistance. A strong advantage of having a metal oxide core is its extreme resistance to plasma etching. To determine etch rates of our resist, etching studies were carried out by first flood exposing a film and then measuring the film thickness with a Woollam spectroscopic ellipsometer. In order to fully exploit the high etch resistance of the metal oxide, an oxygen plasma pre-treatment was applied to the resist before etching. The chemical stability of the ZrO$_2$ core enabled an O$_2$ RIE process for 30 seconds. The film was then
etched for time intervals of 30 seconds with an Oxford 81 etcher, with film thickness measurements being performed between each interval. From these data points, an etch rate of the resist was determined and compared to the etch rate of poly(hydroxystyrene) (PHOST). The etch rate comparisons of ZrO$_2$-MAA and PHOST (polyhydroxystyrene) for CF$_4$ and SF$_6$/O$_2$ are shown in Figure 2 and Figure 3.

With CF$_4$ etch gas, the etch resistance of ZrO$_2$-MAA is six times better than PHOST as shown in Figure 2. The etch resistance of ZrO$_2$-MAA is fourteen times better when etched under SF$_6$/O$_2$ in Figure 3.

The e-beam patterning performance and etch resistance of zirconium oxide nanoparticles functionalized with organic ligands has been reported. Further research is being conducted to fully exploit this material, including different core/ligand variations.

References:


Hafnium and Zirconium Oxide Nanoparticles as Novel Photoresist Materials

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Abstract:
Performance requirements for next generation lithography will necessitate the development of entirely new resist platforms. The new resists for extreme ultra-violet (EUV) lithography must show high etch resistance and high sensitivity. We have developed a novel inorganic photoresist platform to be applied in advanced lithography. These inorganic photoresists are made of metal oxide nanoparticles stabilized with organic ligands and have shown etch resistance that is 25 times higher than polymer resists. This will enable the processing of very thin films (< 40 nm) and will push the resolution limits below 20 nm without pattern collapse.

Summary of Research:
Currently, extreme ultra-violet (EUV) lithography is considered the upcoming next generation patterning technology [1]. Despite remaining challenges with the EUV system, alternative lithographic techniques, such as double patterning, nanoimprint and self-assembly, either cannot achieve the required resolution or have other issues that limit their applicability. As a result, EUV lithography and improved photoresists for this patterning technology are important goals for the semiconductor industry.

As pattern sizes reach the sub-20 nm range, it is necessary to use thinner films to prevent pattern collapse. However, photoresist films that are comprised of organic materials cannot sufficiently resist the etch process as thinner films [2]. Therefore, extremely high etch resistant structures must be studied and developed to allow pattern transfer to the underlying substrate. Additionally, the relatively low intensity of current EUV sources requires photoresists that demonstrate high sensitivity and optimum absorbance. At 13.5 nm, which is the wavelength used in EUV lithography, the absorption of all materials is very strong and only dependent on their atomic composition and density [3]. For example, elements that are commonly used in photoresists at other wavelengths, such as fluorine, are highly absorbing at 13.5 nm making them problematic for EUV applications. Other elements including carbon, silicon, zirconium or hafnium show lower absorption.

In order to fulfill the requirements that were mentioned above, in this study we present a next generation photoresist material based on hybrid organic/inorganic nanoparticles. The nanoparticles are comprised of a hafnium oxide or zirconium oxide core that is surrounded by organic ligands. Previous work at Cornell University has studied the application of these inorganic photoresists in DUV, 193, and e-beam lithography [4]. These studies also revealed that the nanoparticle films exhibit exceptionally high etch resistance due to their thermal and chemical stability [5].

Hafnium oxide nanoparticles stabilized with carboxylic acid ligands were prepared by a controlled hydrolysis reaction. Hafnium or zirconium isopropoxide was dissolved in an excess of the carboxylic acid (methacrylic acid, MAA or isobutyric acid, IBA) at 65°C followed by the slow addition of water. After stirring for 21 hours, the product is precipitated and dried. Photoresist solutions were prepared by adding proper amounts of the nanoparticle powder to PGMEA followed by the addition of the photoactive compound or any other additives. Initial DUV (254 nm) testing was carried out at the Cornell NanoScale Science and Technology Facility (CNF), using an ABM contact aligner equipped with a mercury lamp UV source. EUV experiments were carried out at Lawrence Berkeley National Laboratory (LBNL) using the SEMATECH BMET EUV tool.

The Hf-methacrylic acid (HfMAA) and Zr-methacrylic acid (ZrMAA) inorganic photoresists can be patterned at high resolution using either a photoradical initiator (2,2-dimethoxy...
acetophenone, DPAP) or a photoacid generator (PAG). Additionally, the same films can be patterned either in positive tone or in negative tone depending on the film processing and the choice of developer. This versatility of the inorganic photoresist is demonstrated in Figure 1.

The isobutyric acid nanoparticles can also be patterned at both tones with either DPAP or PAG as the photoactive compound. This is demonstrated in Figure 2 for the HfIBA inorganic photoresist.

The same resist formulations that were patterned using DUV at CNF were then tested under EUV exposure at the LBNL. The ZrMAA nanoparticle photoresist was patterned at 26 nm half-pitch using an exposure dose of 4.2 mJ/cm². The results demonstrate that the inorganic photoresist has a remarkable sensitivity and the capability for high resolution patterning.

References:


Figure 1: Positive and negative tone DUV patterns using the inorganic photoresist with a PAG additive: A) HfMAA, positive tone, B) HfMAA, negative tone, C) ZrMAA, positive tone, and D) ZrMAA, negative tone.

Figure 2: Positive and negative tone DUV patterns using the HfIBA system: A) positive tone using DPAP, B) negative tone using DPAP, C) positive tone using PAG, and D) negative tone using PAG.
Nanocalorimetry Study of Metastable Au-Si Alloy

CNF Project Number: 522-94
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Abstract:
This project focuses on the applications of the thin film nanocalorimetry device [1, 2] developed using CNF. We investigate interesting thermodynamic properties that are unique to nanometer size materials including size-dependent melting point depression and magic number size formation in metal nanoparticles [3], thickness dependent glass transition in polymer thin films [4], phase transitions in self-assembled monolayers of alkanethiols (SAMs) [5], and the melting of lamellar crystals of silver alkanethiolates (AgSR) [6, 7]. In this report, we discuss the formation of a unique metastable Au-Si alloy ($\delta_1$) through the in situ nanocalorimetry measurement during physical vapor deposition (PVD) of gold (Au) and silicon (Si) [8]. The $\delta_1$ melts 60K lower than the eutectic alloy and has a composition of 74 ± 4 at. % Au and a $b$-centered orthorhombic structure ($a = 0.92$, $b = 0.72$, and $c = 1.35$ nm; body-center in the $a$-$c$ plane), which grows heteroepitaxially to Au.

Summary of Research:
We have studied the formation of a unique metastable phase ($\delta_1$) which melts ~ 60°C below the eutectic melting point (305°C vs. 363°C) in the gold-silicon (Au-Si) system using in situ nanocalorimetry measurement during the deposition of Au and Si. This is a rare case of a direct thermal analysis a metastable alloy and to our knowledge the first measurement in the Au-Si system. Figure 1 shows the schematic of nanocalorimetry device and the formation of $\delta_1$ on a nanoparticle gold substrate wherein the metastable alloy grows heteroepitaxially with gold and wets the surface. The nanocalorimetry result shows the melting peak at 305°C, which is lower than the $\gamma$ phase, the eutectic, or the 2D surface crystal.

The results of the in situ nanocalorimetry during the deposition of Au and Si are shown in Figure 2. Figure (2a) shows the result when the sample is initially silicon rich where Si is deposited first and then Au is added while the nanocalorimetry measurement is being taken at the same time with the resolution of submonolayer of added Au. The results show the initial formation of the eutectic, but after more Au is added, the $\delta_1$ phase dominates. Both the eutectic and $\delta_1$ show size-dependent melting point depression. Figure (2b) shows...
the opposite case wherein Au is deposited first and then Si is added. Both the eutectic and $\delta_1$ form, and no significant melting point depression is observed at the initial stages of the reaction due the difference in the wettability of $\delta_1$ on Au and Si. The $\delta_1$ does not wet a Si surface, so it forms small 3D particles — while it wets an Au surface, so it forms a uniform 2D surface layer (confined liquid). Geometrical considerations explain why the size dependent melting point depression is more significant in a 3D compared to a 2D structure.

The schematic on Figure 3 shows the key learnings from this investigation. The metastable $\delta_1$ alloy grows heteroepitaxially to a gold substrate. Upon melting, the liquid phase features a high degree of ordering of the atoms. This ordering is brought about by the 2D crystalline surface layer, the layered liquid induced by this surface ordering, the ordering at the interface of the liquid to the Au substrate and the layered liquid induced by this interfacial ordering. The metastable solid $\delta_1$ phase is the frozen state of this highly ordered liquid.

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**References:**


**Figure 2:** Three dimensional $C_p(T, t)$ caloric maps during; (a) Au deposition with the sample initially Si-rich, and (b) Si deposition with the sample initially Au-rich. Eutectic forms first in (a) followed by $\delta_1$ (Si-rich to Au-rich), whereas $\delta_1$ forms first in (b) followed by the eutectic (Au-rich to Si-rich). Both $\delta_1$ and eutectic are present in Si-rich samples beyond the thickness range shown in (b). Insert in (a) shows the TEM micrograph of Au and Si particles with $\delta_1$ at the interface. Insert in (b) is a $C_p(T)$ plot showing solidification (exothermic) of liquid after $\delta_1$ melts, which occurs in the presence of Au(s) and Si(s).

**Figure 3:** Schematic diagram of solid $\delta_1$ and liquid Au-Si alloy on gold substrates. Liquid Au-Si shows the 2D surface freezing with the same lattice parameters as $\delta_1$, and the ordering within the liquid due to both the crystalline surface and the Au/(Au-Si) interface.
Patterning of Polymer Brushes as Membranes and Investigating the Effects

CNF Project Number: 640-97
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Abstract:

Patterning of polymer films has been an area of great interest due to the broad range of applications including bio-related and medicinal research. Consequently, the nature of patterned polymer brushes as removable thin films was explored. Both an etching and polyvinyl alcohol dissolution process has enabled us to lift off very thin membranes for further characterization with the potential of using them as Janus membranes for biological applications. Furthermore, the repolymerization of monomer on brushes that had previously been exposed and patterned was explored.

Summary of Research:

Polymer brushes can be formed by densely attaching polymer chains to a substrate. They have garnered much attention due to the need for systems in the fields of microelectronics, nanofluidic devices, biosensing, and other areas of nanotechnology [1-4]. Another application of interest is the production of Janus membranes. We have begun to explore different means for detaching polymer brush membranes from a surface. Previous work on polymer brush nanochannels led us to question the robustness of the bridging polymer film that stretched over distances ranging from 100 nm to a few microns. The first method involved a silicon oxide layer upon which the polymer brushes were grown from via atom transfer radical polymerization (ATRP) to thicknesses ranging from 30 to 70 nm. The polymer brushes were then patterned and crosslinked by a UV source and etched with HF to produce very thin membranes. HF was chosen because it etches only the silicon oxide and does not harm the polymer brush membranes, and because silicon oxide is a conventional surface for polymer brush growth. Thus we are not limited to the types of brushes membranes that can be produced.

Membrane characterization included TEM and optical microscopy (Figure 1). Results indicate the membranes retain a significant amount of strength even at very thin thicknesses. Folding, wrinkling, and bending are commonly observed instead of tearing or falling apart and therefore imply that membranes are robust enough to undergo further functionalization to produce Janus membranes. Additionally, this technique can provide information regarding ATRP initiator immobilization as well as the brush polymerization process to answer questions about the nature of brush films.

A second method for the controlled release of polymer brushes from a silicon substrate involves crafting the polymer film from a sacrificial layer of poly (vinylalcohol) (PVA). For this, thin layers of PVA were spin-coated on bare silica and were subsequently functionalized with an ATRP starter in a gas phase reaction. ATRP polymerization of monomers like styrene or methylmethacrylate yielded homogenous polymeric films with thicknesses between 20 and 200 nm linked to the PVA. Subsequent polymerization of a second monomer allowed producing Janus films consisting of two different brush layers. After patterning these films into isolated squares with lateral dimensions of $10 \times 10 \mu m$ using photolithographic techniques, the PVA layer was dissolved in water. Thereby, the patterned polymer brushes were lifted.
off the substrate and formed a dispersion in the water. Due to entanglements between remaining PVA chains and the polymer brush, the resulting particles were stable without further crosslinking. They were characterized using optical-, fluorescence- and electron microscopy (Figure 2). Currently, we are investigating the possibility to use these nanofilms as encapsulation agents.

In order to expand our range of patterning techniques, we investigated the possibility of patterning positive tone polymer brushes using deep-UV photolithography. In comparison to recent experiments using e-beam lithography [5], this approach allows patterning larger brush areas at lower costs. In first experiments, we exposed brushes from several materials like poly (methylmethacrylate), poly (isobutylmethacrylate) and poly (neopentylmethacrylate) at different doses of 220 nm irradiation. After development, optical and scanning probe microscopy proved that the patterning was successful. Additionally, we investigated the effect of irradiation on the brush’s ability to reinitiate ATRP polymerization. For this, we polymerized styrene on deep-UV patterned brushes. We found that the ATRP polymerization runs much slower in exposed areas of the brush, thus drastically increasing the contrast of the first pattern. Consequently, this new patterning technique allows the patterning of negative tone materials like polystyrene without the application of photoresists. Finally, applying a gray-scale exposure gradient enabled us to produce interesting thickness gradients in polymer brushes.

Acknowledgements:
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References:
Characterization of Molybdenum Disulfide Devices

CNF Project Number: 804-99
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Abstract:
We theoretically and experimentally investigate molybdenum disulfide (MoS₂) for transparent electronics. Using a first principles approach, we determine the plane where charge transport is occurring. Next using optical spectroscopy we determine the number of layers in preparation for fabrication of Hall and field effect devices. Finally we measure the fabricated devices and estimate their properties.

Summary of Research:
Recently there has been increasing interest in flexible transparent electronics in order to maintain industry growth following the theme of “More than Moore.” However getting transparent high performance devices on transparent substrates remains a challenge due to non-ideal transport properties of organic electronics. Here we propose using the recently rediscovered transition metal dichalcogenides for this purpose, of which MoS₂ is one example. These materials are transparent due to their inherent thickness. Furthermore they are semiconducting and have a direct bandgap. We can then think about scaling these devices further than 3D materials since the electrostatic integrity can be maintained for shorter channel lengths. Finally by having a direct bandgap we can think of on chip optical devices. Although MBE technology for these materials is still in its infancy we can investigate their properties to first order using exfoliation techniques and first principles calculations.

We first determine where the charge transport is occurring in the plane of MoS₂ as this has significant implications for device performance and reproducibility. In our calculation we assume the LDA approximation with 30 by 30 k-point grid sampling and an energy cut-off of 100 Rydbergs. We use the quantum espresso solver to solve for the DOS and band structure. Based on our calculations we observe a direct bandgap of 1.78 eV and the density of states near the Fermi level is peaked at the p orbital of the Mo atom as shown in Figure 1. We can conclude that charge transport is occurring in the plane of the Mo not at the surface of the sheet.

Next we wish to fabricate some devices to investigate the carrier type and concentration. It is important to ensure we have a monolayer because the bandgap is indirect for bulk MoS₂ so the properties will be qualitatively different. To this end we perform Raman, AFM, and photoluminescence scans of the exfoliated flake before fabrication. The thickness we obtain for our exfoliated flakes is around 1 nm. The difference between the Raman (Figure 2) and photoluminescence (Figure 3) is that while Raman is a resonant process, photoluminescence is not. The photoluminescence spectra for a bilayer has a peak due to a nearby band valley as well as a reduced photon count due to indirect bandgap.

In contrast MoS₂ monolayer has a higher peak due to the direct bandgap and no secondary peak. For the Raman spectra, the phonon modes corresponding to the peaks can be found in Ref. 1. In this case the difference between the layers are harder to discern because the layers are only weakly coupled and each layer has similar phonon modes. Nonetheless the in-plane E₂g and out-of-plane A₁g modes stiffen as additional layers are added, and this shows up as a shift in the Raman spectra as shown.

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Figure 1: MoS₂ projected density of states.
After ascertaining the number of layers, we employed e-beam lithography to fabricate our devices because of the size of the flake we needed the resolution and overlay afforded by e-beam lithography. The substrate is 285 nm SiO₂ and the contacts are 5 nm Ti and 50 nm Au. We fabricated a Hall device and measured the source drain current across it with gating.

Based on our estimate, our device impedance to be 0.8 MΩ for a 1 μm device. This implies that our device is largely limited by the contact resistance. We plan to try different contact materials as well as anneal the contacts to reduce the contact resistance in our current runs.

In conclusion we have performed preliminary studies of MoS₂ both from first principles and experimentally. We find that MoS₂ might have potential for transparent electronics but needs further investigation of electrical transport.

References:
Structure and Motion of Stacking Faults in CVD-Grown Bilayer Graphene

CNF Project Number: 900-00
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Abstract:

We use diffraction-filtered darkfield transmission electron microscopy (TEM) to study the structure and motion of stacking faults in Bernal-stacked bilayer graphene. We find that corrugations in the original copper growth-substrate correlate closely with AB-BA stacking faults and that additional faults occur at what are presumed to be high stress regions, perhaps during the process of transferring these to TEM grids. We observe the dynamics of these AB-BA boundaries and find that they have nanoscale fluctuation at room temperature on a time-scale of minutes.

Summary of Research:

Monolayer and bilayer graphene—one and two atom-thick sheets of graphite, respectively—have received much attention over the past decade as materials exhibiting superlative electronic and mechanical properties. Part of their appeal to physicists has been in their simplicity as prototypical two-dimensional materials. However, the fact that these materials are often grown and/or studied on a three-dimensional substrate adds a complexity to the system which, while undesirable for many device applications, yields a fascinating and not-yet exploited opportunity for the study of the structure and motion of defects in a simple and easily visualized system. Here we use darkfield transmission electron microscopy to image the structure and motion of stacking faults in bilayer graphene and relate these to both the original growth substrate and transfer process.

Large-grain (30-100 µm) graphene was grown on copper foil (Alfa Aesar Cat#13382), by chemical-vapor deposition (CVD), using the Ruoff group’s enclosure method [1]. In this method, the copper growth foil is enclosed in a second copper foil to limit exposure to growth gases, and placed in an evacuated furnace (base pressure 10^-4 torr). Methane is then flowed at 3 sccm, and hydrogen is flowed at 60 sccm at 980°C for two hours, then cooled. The resulting graphene is predominantly monolayer, with ~ 10 µm six-fold symmetric star-shaped bilayer and multilayer patches at many of its nucleation sites.

Figure 1 shows one of these bilayer regions as imaged by scanning electron microscopy (SEM), and atomic force microscopy (AFM). In the SEM image on the left, the darker hexagon corresponds to bilayer on copper, while the rest of the visible surface is covered in monolayer graphene. As can be seen in the topographic AFM image on the right, the copper surface underneath these bilayer patches tends to be more corrugated than the surrounding monolayer.

On this sample, bilayer corrugations are ~ 10 nm high with a ~ 200 nm separation, while monolayer corrugations are ~ 3 nm high with a 100 nm separation. Due to the alternating positive and negative curvature across these corrugations, we might expect bilayer graphene to have AB-BA stacking faults parallel to these corrugations.

To investigate this, after imaging the graphene on copper by SEM, we spun 50 nm of PMMA on it, etched away the copper, transferred the PMMA and graphene to a carbon...
Quantifoil TEM grid, and baked it at 300°C for three hours to remove the PMMA. By using darkfield TEM, with an aperture in the diffraction plane selecting electrons diffracting from the graphene lattice in a particular direction, we are able to distinguish the two different mirror-symmetric stackings of bilayer graphene (AB and BA) [2].

Figure 2 shows the results of such a darkfield TEM measurement on a region of bilayer graphene that we had previously imaged by SEM while on its original copper growth substrate. In the upper left of the bilayer region, we notice vertical AB-BA stacking faults which seem to correspond to the vertical corrugations in the copper surface in the upper-right SEM image. Additionally, we see that near the indentations in the star-shaped bilayer which are expected to correspond to regions of high stress (marked by S’s), there is a high concentration of stacking faults that propagate inwards to the center of the bilayer patch in the bottom right. In this and many other samples, it seems that the stacking faults observed in CVD-grown and subsequently-transferred bilayer graphene samples are a combination of faults caused by stress during transfer, and those that occurred due to interaction with the original growth substrate.

To investigate how stable these boundaries are at room temperature, we zoom in on a bilayer region that has a high density of faults. Figure 3 shows a series of darkfield TEM images taken over the course of 43 minutes. By filtering for one of the outer diffraction spots, we are able to distinguish the AB-BA transition boundaries (faults), which appear black, from the brighter Bernal-stacked (AB or BA) regions on either side. Over the course the measurement, all of these boundaries fluctuate back and forth on a minute time-scale, and a few nanometer length-scale. The white arrows indicate a few boundaries that have shifted by more than 10 nm.

In this work, we have presented a few measurements demonstrating the origin and dynamics of faults in bilayer graphene, and have highlighted bilayer graphene as a model two-dimensional system for studying the structure and dynamics of crystalline faults.

References:
Design and Validation of High-Efficiency Chopper for Magnetoresistive Sensors

CNF Project Number: 1236-04  
Principal Investigator: Prof. R. Bruce van Dover  
User: Huanan Duan

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Primary Source of Research Funding: Welch Allyn  
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Abstract:
Low-frequency (1/f) noise severely limits the low-frequency performance of magnetoresistive sensors. Based on reluctance analysis and finite-element simulations, this paper reports a high-efficiency chopping system consisting of a flux concentrator and chopper to mitigate the effect of 1/f noise and improve the field sensitivity for magnetoresistive sensors. Experimental results based on the optimized design using an anisotropic magnetoresistance sensor validate the concept. The sensitivity of the sensor with the chopper at OFF and ON positions is determined to be 0.009 and 0.067%/Oe, respectively, which yields a high sensitivity chopping efficiency, namely 72%.

Summary of Research:
Ultra-high-sensitivity magnetic sensors with a magnetic field detection limit in pT/Hz^{1/2} region have aroused renewed research interest in recent years due to the discovery of novel device structures with large magnetoresistance (MR), such as magnetic tunnel junctions (MTJs) [1, 2] and spin valves [3]. Intrinsic noise is an important property to obtain high signal to noise ratios (SNR). While the frequency-independent white noise sets the ultimate limit to the SNR, 1/f noise dominates in the low frequency region (< ~1 kHz), and severely inhibits the potential application of MR sensors in these region. In this paper, we report a novel chopper design to suppress the 1/f noise, in which the only moving part is a small, low-mass bar that acts as a low-reluctance magnetic short. We validate the optimized design by experiments using anisotropic-MR (AMR) sensors and demonstrate a chopping efficiency of 72%.

AMR stacks were deposited on 3-inch SiO_{2}-coated Si substrates using DC magnetron sputtering with a base pressure below 5 × 10^{-9} Torr. The stack consists of Si/SiO_{2}(500)/Ni_{0.81}Fe_{0.19}(25)/Ta(8) (thicknesses in parentheses are in nm). A micrometer thick Py layer was electrodeposited on an area defined by photolithography to make the FCs and chopper elements [4]. The geometry of the chopping system is shown in Figure 1. The distances between the FCs and the shorting bars were set to be 2 µm (OFF position) and 80 µm (ON position). AMR sensors are 20 µm wide and 100 µm long.

The as-fabricated devices were annealed at 240°C (heating rate: 20°C/min) in Ar flow (flow rate: 80 sccm/min) for 30 minutes and cooled down under a magnetic field of 150 Oe to set the easy axis perpendicular to the long side of the shorting bar [5]. AMR sensors were measured using a multimeter with 1 mA current bias at room temperature in a magnetic field ranging from -40 ~ 40 Oe. The MR ratio was defined as (R_t-R_l)/(1/3R_l+2/3R_t)*100, where R_l and R_t are the longitudinal and transverse resistances, respectively.

In Figure 2a, the MR of the sensor with and without FCs is recorded as a function of the external magnetic field applied parallel to the short axis of the AMR sensor. Clearly, the MR curve is symmetric and hysteresis free. Figure 2b shows the effect of FCs on the MR curves. Here the sensors are 45° with respect to the direction of the external
magnetic field, which leads to decrease of the MR value from 0.76% to 0.23% and asymmetry of the MR curves.

Figure 3 presents the effect of FCs and chopping system using the optimal design parameters on the MR-H curves of AMR sensors. The field sensitivity of the AMR sensors is defined as MR/H_{sat} and can be obtained directly from the MR-H curves [6]. From Figure 3a, the field sensitivities of the AMR sensor with and without FCs, namely S_{FC} and S_{AMR}, can be determined to be 0.081 and 0.008%/Oe, respectively, which yields a gain of 10. This confirms the function of FCs to enhance the magnetic flux.

In Figure 3b, the MR-H curve is steeper with the chopper in ON position compared to that with the chopper in OFF position. This implies that with the same external magnetic field change the chopper in OFF position results into smaller resistance change and subsequently smaller sensitivity due to the shunting effect of the chopper. We can define a sensitivity chopping efficiency, η_s, as (S_{ON}-S_{OFF})/S_{FC} * 100%, where S_{ON}, S_{OFF}, and S_{FC} are sensitivity with the chopper in ON position, OFF position, and with no choppers, respectively. The sensitivities for OFF and ON positions, S_{OFF} and S_{ON}, are determined to be 0.009 and 0.067%/Oe, respectively. The sensitivity with the FCs only (S_{FC}), by contrast, is 0.081%/Oe. So η_s is determined to be 72%.

Our results herein present the best case scenario and they validate the high-efficiency chopper design.

References:
Colloidal Self-Assembly-Directed Laser-Melt-Induced Crystalline Silicon Nanostructures

CNF Project Number: 1356-05
Principal Investigator: Ulrich Wiesner
User: Kwan Wee Tan

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Abstract:
We describe a rapid, facile technique coupling colloidal crystal templating with laser thermal processing to fabricate crystalline Si nanostructures with deterministic non-close-packed symmetry. Two- and three-dimensional (2D, 3D) colloidal crystals are grown as porous templates on a single-crystal Si substrate. Pulsed excimer laser irradiation is used to induce a transient melt-crystallization conversion of the amorphous silicon filled in the templates to the crystalline phase. The pattern transfer yields are high and long-range hexagonal order is maintained. The method is highly adaptable as an alternative strategy to generate silicon nanostructures of other symmetries for use in applications such as energy generation and storage.

Summary of Research:
Ordered nanostructures based on silicon grown by colloidal self-assembly have been extensively studied and widely adapted for nanofabrication and many potential applications, for example, photonic crystals and solar cells [1-7]. In particular, non-close-packed crystalline silicon nanostructures are highly desirable for their enhanced electrical conductivity, photonic and other surface properties [5-10].

In this work, we combined colloidal crystal template formation with laser thermal processing to generate crystalline silicon (c-Si) nanostructures with non-close-packed symmetry [11]. Figure 1 schematically shows the experimental procedure.

We began by growing a hexagonally arranged close-packed (hcp) monolayer colloidal crystal of 350 nm or 530 nm polystyrene (PS) spheres surrounded by silica (SiO_2) using the vertical deposition method. The latex beads were calcined in air at 500°C, leaving behind a highly ordered SiO_2 inverse monolayer. The SiO_2 template was subsequently filled with a 100 nm thick amorphous Si (α-Si) overlayer and irradiated with a 40 ns full-width-half-maximum pulsed XeCl excimer laser (308 nm wavelength) in air to induce the transient melt conversion of α-Si to the crystalline phase (~ 20-100 ns).

Finally, the template was removed in concentrated hydrofluoric (HF) acid solution, leaving hexagonally arranged non-close-packed (hncp) Si nanostructured array as seen in Figure 1c. Using the 530 nm PS colloidal template with a single laser irradiation pulse at 600 mJ/cm^2, we grew 2D hncp arrays of c-Si nanostructures with an average width and height of around 410 and 300 nm, respectively.

Figure 2 shows the hncp c-Si nanostructures generated from a smaller, 350 nm PS colloidal template and four sequential
laser pulses at 500-700 mJ/cm², with an average width of 170 nm and height of 60-70 nm height. Atomic force microscopy analysis indicated a ~100% hexagonal pattern transfer from the (350 nm) cp SiO₂ inverse colloidal template to the ncp c-Si nanostructures.

The method is easily adaptable to generate more complex 3D ordered macroporous c-Si inverse opals with hncp symmetry. We began with a ~150 nm thick plasma enhanced chemical vapor deposited (PECVD) α-Si in a (350 nm) multilayered SiO₂ inverse colloidal crystal template. The SiO₂/α-Si core-shell composite inverse opal was subsequently irradiated with a total of 43 sequential laser pulses at fluences from 5-550 mJ/cm². Selective HF etching of the SiO₂ template results in a ~1.3 μm thick c-Si single interconnected network of hncp inverse opal morphology, see Figure 3.

In conclusion, we have demonstrated a rapid and highly versatile method using colloidal crystal templates coupled with pulsed excimer laser-induced melting to obtain ncp c-Si arrays of varying scales at ambient conditions. In analogy to results on block copolymer templates, this approach may also be applied to form not only single-crystal homoepitaxial but also heteroepitaxial ncp nanostructured arrays on Si, enabling new functionalities and the engineering of novel device prototypes [12].

References:
Ionic Conductivity in Thin Film Y-Zr-Oxide

CNF Project Number: 1400-05
Principal Investigator: Prof. R. Bruce van Dover
Users: Chao-Chen Yuan, Natalie Becerra, Dr. Huanan Duan, Dr. John M. Gregoire

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Abstract:
We have demonstrated the validity of high-throughput measurements of ionic conductivity in oxygen-ion conductors. Y-Zr-O composition-spread thin films were prepared by reactive RF co-sputtering. Lithographically-defined planar interdigitated electrodes allow us to infer the conductivity with good accuracy. The intragrain oxygen ion conductivity of thin film was systematically measured as a function of yttria concentration over the range 2 mol % to 12 mol %; the results are consistent with measurements on bulk materials reported in the literature. Validation of this technique means that it can now be applied to novel chemical systems for which systematic bulk measurements have not been attempted.

Summary of Research:
The development of solid oxide fuel cells (SOFCs) into a common commercial technology remains limited by the elevated operating temperatures required for ionic conductivity in the cell electrolyte. Two classes of cells are considered: conventional large-scale (megawatt-range) devices operating at 600-1000°C, and small thin-film-based (watt-range) devices operating at < 500°C. In either case, operation at lower temperature is desirable, but not feasible because the thermally-activated motion of O₂⁻ ions becomes too sluggish. We are developing the techniques needed to explore new materials for these applications.

Our approach is to prepare compositionally-graded thin films and characterize the bulk (intragrain) ionic conductivity as a function of position. In a single experiment we can potentially determine the ionic conductivity of hundreds of compositions. This project focused on validating the technique—demonstrating that we can reliably measure conductivities in a well-documented model chemical system, Y-Zr-O. Addition of sufficient Y to monoclinic ZrO₂ stabilizes the cubic phase, hence this system is referred to a “yttria-stabilized zirconia” (YSZ).

YSZ composition-spread thin films were deposited on 75 mm Φ Si or SiO₂ substrates by reactive RF co-sputtering using elemental Zr and Y targets [1]. The composition gradient was roughly 0.25-1 at% per mm and the films are roughly 150 nm thick. The films were annealed in air at 1000°C for one hour to achieve good crystallinity and to preclude significant structural changes during conductivity measurements at ~ 500°C. For electrical measurements, two electrode configurations (see Figure 1) were tested, namely the out-of-plane and in-plane (interdigitated electrode, IDE) geometries. Counterelectrode dots (Figure 1, left) were 200 µm Φ Pt deposited by evaporation using a metal shadow mask. IDEs were created using photolithography with finger length, width and interelectrode spacing set to 750 µm, 5 µm and 5 µm, respectively. Devices were created on 1 mm centers covering the substrate.

Devices were measured in a custom-built high-temperature probe station with better than ± 3°C uniformity, using micromanipulators to position Pd-needle probes on the contact pads. The ionic conductivity was evaluated using electrochemical impedance spectroscopy (EIS) measurements in the air ambient using an LCR meter at frequencies ranging from 100 Hz to 1 MHz. The complex impedance, Z, is then fitted to a model to extract the ionic conductivity. Figure 2 illustrates typical data obtained for Zr₀.₉₆Y₀.₀₄O₁.₉₈ at 440°C using a Nyquist plot (-Im(Z) vs. Re(Z)) with frequency as

Figure 1: Schematic of (a) out-of-plane configuration and (b) in-plane (interdigitated) configuration for electrical measurements.
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a parameter. Parallel-plate capacitor (“out-of-plane”) and IDE (“in-plane”) devices yield values for Z due that are different not only in scale because of the different geometric proportions, but also in shape due to the difference in electrode spacing. The solid lines in Figure 2 represent model fits, where the circuit model is indicated in the inset. It is readily apparent that the IDE device fits the model well, while the parallel-plate device evidently requires a more sophisticated model. The resistances $R_1$ and $R_2$ correspond to the ionic motion associated with intragrain and intergrain conductance, respectively. The circuit elements denoted $Q$ represent “constant-phase behavior” used to model the distribution of activation energies associated with ionic motion.

Figure 3 shows the intragrain O-ion conductivity inferred for our YSZ composition spread film as a function of composition (open symbols), as measured at 440°C. For comparison, measurements reported for bulk single-crystal [2] and polycrystalline-ceramic [3] samples are shown as solid symbols. The agreement is excellent. Our measurements represent only the first step in identifying a good oxygen-ion conductor: follow-up studies would be needed to confirm that the conductivity is due to ions rather than electrons, to characterize the temperature dependence of the conductivity, to characterize the intragrain conductivity, etc.

This work [4] demonstrates that reliable measurements of ionic conductivity can be made using codeposited composition-spread thin films, in that the measurements yield values that are consistent with the intragrain conductivity reported for bulk samples. This approach allows high-throughput measurement of behavior over a wide range of compositions with 0.5 mol% resolution in multication oxide systems. We used YSZ as a model system, varying the yttria concentration over the range 2 mol% to 12 mol% $Y_2O_3$. The in-plane electrode configuration was found to be more suitable than out-of-plane configuration measurements on 150 nm films. The intragrain ionic conductivity of the YSZ thin films is essentially identical to that of bulk specimens, with a peak conductivity value of about $3 \times 10^{-4}$ S cm$^{-1}$ at 440°C for the optimum $Y_2O_3$ concentration near 8 mol%.

References:


Electrical Characterization of Nanocrystal Arrays

CNF Project Number: 1645-08
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Abstract:
Notwithstanding the rapid progress in nanocrystal-based prototype devices, significant knowledge gaps concerning the electronic structure and charge transport in nanocrystal thin films remain. Phenomenological models adopted from transport in bulk semiconductors have enabled much of the progress to date; however, these models are less satisfying with regards to mechanistic clarification as they do not adequately address interfacial transport in coupled quantum confined systems. This knowledge gap is likely to impair future advances in nanocrystal based devices. We apply advanced optical and electrical characterization techniques to achieve a deeper understanding of charge transport in nanocrystal films.

Summary of Research:
We have studied charge transport in PbS NC films that coupled via chemical treatment with ammonium sulfide. Temperature-dependent mobility measurements reveal decreasing mobility with increasing temperature. In contrast to thermally activated hopping, this trend has previously been interpreted as ‘band-like’ charge transport through delocalized states. However, the electronic disorder in NC films is too large to support the interpretation as in terms of band conduction.

The effect of temperature on carrier concentration on the other hand is not yet well understood and is likely to impact the negative temperature coefficient of the charge mobility. Our current experiments aim to clarify this effect.

Another critical unresolved question is: ‘What limits the mobility of charges through highly coupled nanocrystal films?’

The answer to this question has important implications both on understanding the basic charge transport mechanism as well as on the performance limits of nanocrystal thin film in photovoltaic devices.

Charge trapping is commonly cited as the cause of low mobility for localized carriers and hopping transport, but this does not adequately describe the limitation in ‘band-like’ transport. We have adopted a model of charge transport in polycrystalline thin films to describe the charge transport limitation in context of grain boundary scattering. This model predicts charge transport limited by acoustic phonon scattering at high temperatures and a $\mu \sim T^{-5/2}$ temperature dependence; at low temperatures grain boundary scattering dominates.

Our current work focuses on refining this hypothesis by testing NCs with controlled superstructure and degree of interconnection; this builds on recent advances in our group to create superstructures with controlled symmetry and degree of connection.
Development of a Monochromatic Phonon Source for Studying Nanoscale Phonon Heat Transport

CNF Project Number: 1746-09
Principal Investigator: Richard D. Robinson
Users: Obafemi Otelaja, Jared Hertzberg, Mahmut Aksit, Derek Stewart

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Primary Source of Research Funding: Start-up Funding, KAUST-Cornell Center for Energy and Sustainability, National Science Foundation Agreement No. DMR-1149036, DOE Office of Basic Energy Science under Award Number DE-SC0001086

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Abstract:
Thermal transport by acoustic phonons in nanoscale dimensions differs markedly from behavior in bulk materials because of the phonons’ interaction with surfaces and interfaces. To improve our understanding of such effects, we are developing a microfabricated phonon spectrometer. We have demonstrated a prototype of such a device, generating a controllable, non-thermal distribution of acoustic phonon modes ranging from ~ 100 to ~ 800 GHz and measuring its transmission through silicon microstructures and nanostructures at a temperature of 0.3K. To generate and detect the non-thermal phonons, we exploit excitation and decay processes in superconducting tunnel junctions (STJs) attached to the micro/nanostructures. By these studies, we seek to understand thermal transport at the nanoscale in order to improve the efficiency of nanostructured thermoelectric materials.

Summary of Research:
Phonon spectroscopy using superconducting tunnel junctions (STJs, consisting of two superconducting metal films separated by a tunnel barrier) has been described by Kinder, et al. [1]. To probe ballistic phonon transport in silicon, we construct devices in which an STJ phonon generator and detector face each other across a microstructure (Figure 1). We first perform shallow KOH etch of a <100> silicon wafer to form ‘mesa’ type microstructures 0.8 µm high, 200 µm long and 7 to 30 µm wide (Figure 2). To attach STJs in contact with the mesa sidewalls, we perform photolithography using the GCA 6300 DSW 5X g-line stepper, followed by deposition of two thin films of aluminum separated by an in situ-grown oxide barrier (performed in a dedicated evaporating chamber outside of CNF), followed by lift-off of the photoresist. We form 112 chips per wafer and twelve devices on each chip.

Figure 1: Schematic diagram of direct ballistic phonon measurement.
Figure 2: SEM image of phonon emitter and detector attached to silicon micro-mesa.
We form the phonon detectors in a split ‘SQUID’ type geometry (Figure 2) to enable suppression of Josephson currents during measurement.

We have tested the devices at a temperature of 0.3 K in a helium-3 refrigerator [2]. The emitter STJ is biased at voltages greater than twice the aluminum superconducting bandgap of 170 microeV, thereby injecting free electrons into excited states of the superconductor. Decay of these excited states emits a highly non-thermal distribution of phonons, which the STJ radiates into the adjacent silicon. The phonon spectral distribution comprises a monochromatic component at an energy of ~ 340 micro eV plus a broad distribution having cutoff energy determined by the bias voltage. Modulation of the bias voltage therefore allows the phonons at this cutoff energy to be isolated in the measurement, offering spectral resolution as low as ~ 10 GHz over a range of hundreds of gigahertz. The detector STJ functions by collecting incident phonons and measuring a tunneling current of the locally-excited electrons. We confirm the non-thermal nature of the phonon distribution by observing a step-change in signal level at a generator voltage four times the superconducting bandgap, and confirm direct ballistic transport by selectively blocking the direct path through the silicon (Figure 3).

In upcoming measurements, we seek to force the phonon flux to traverse silicon nano-channels in order to reach the detector (Figure 4). We form the nano-channels using electron-beam lithography (JEOL JBX-6300FS) followed by DRIE plasma etch (Unaxis 770). By observing the dependence of the transmission on phonon frequency, we will determine the mean free path of the phonons in such nanostructures and relate this to both phonon wavelength and nanostructure geometry, thereby improving fundamental understanding of phonon-mediated thermal transport in nanostructures.

References:
**Vertically Aligned Carbon Nanotube Membrane for Solar Hydrogen Generation**

**CNF Project Number: 1782-09**  
**Principal Investigator: Prof. Todd D. Krauss**  
**User: Gregory Pilgrim**

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*Primary Source of Research Funding: US Department of Energy*  
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**Abstract:**
Vertically aligned carbon nanotube (VA-CNTs) membranes for an artificial photosynthetic device were synthesized. Fabrication of VA-CNTs proceeds by chemical vapor deposition (CVD) at 800°C. Following nanotube growth, an epoxy is spin-coated onto the array to make a self-supporting, chemically resistant, and electrically conductive membrane.

**Summary of Research:**
The development of new energy sources is a necessity for satisfying the increasing worldwide demand for energy. Out of the possible energy resources, the sun is the most widely available and most abundant source for long-term carbon free energy. However there are still many challenges in making solar energy viable economically and socially [1, 2]. In this project, we are developing vertically aligned carbon nanotube membranes for a bio-and nano-inspired integrated system for producing hydrogen from solar energy. VA-CNTs will act as a linkage between a light harvesting bio-molecule and hydrogen producing catalysts. Due to their exceptional electrical properties, NTs can efficiently accept and separate electrons from the photo-excited donor and transport them to the catalyst even over long distances. At the same time, the impermeable VA-CNT membrane can provide a physical barrier between the light harvesting and hydrogen producing components, separating them into different chemical environments.

Dense forests of vertically aligned carbon nanotubes were synthesized by chemical vapor deposition (CVD). Catalyst layers of 5-10 nm of Al₂O₃ followed by 3-12 nm of Fe are deposited on a Si wafer by e-beam evaporation. The thin iron layer is annealed at 800°C under a hydrogen flow [3]. Al₂O₃/Fe form catalyst particles that are 8-12 nm as analyzed with atomic force microscopy (AFM). These particles seed CNT growth at 750-800°C when in an environment comprised of a carbon source (ethylene) and a carrier gas (argon).

The CNT forming reactions are carried out in a single joint tube furnace [4] where the VA-CNTs grow to heights of 100-150 µm (Figure 1). After growth, the VA-CNTs are coated with a commercially available two part epoxy (Figure 2) such that the bulk NT array is completely coated, while ~ 10 µm of CNT tip are left exposed (Figure 3). The exposed NTs are therefore available to conduct electrons, and in fact, we verified through current-voltage spectroscopy that electron transport through the array was Ohmic. The resulting self-supporting membranes exhibit a trans-membrane resistivity on the order of 0.1Ω/µm. As CNTs have already been shown capable of transporting ions [5] future work is aimed at facilitating proton conduction, as a material capable of transporting electrons and protons would be a significant step towards solving the water splitting problem [6].

**References:**
Figure 1: SEM image of vertically aligned carbon nanotubes.

Figure 2: SEM of the epoxy penetrating fully into the NT array.

Figure 3: SEM image of carbon nanotubes exposed above the epoxy-coated array.
Calculation of the Temperature Dependent Superconducting Superheating Field

CNF Project Number: 1959-10
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Abstract:
Modern accelerators use superconducting radiofrequency (RF) cavities to accelerate particles. These cavities are typically operated well above the critical magnetic field at which it is thermodynamically favorable for the flux to penetrate the superconductor. However, an energy barrier to flux penetration allows cavities to operate in a meta-stable, superheated state. The superheating field is the point at which this barrier vanishes, allowing flux to enter the superconductor, and represents a fundamental limit to the operation of superconducting RF cavities. This work is a numerical calculation of the superheating field using the semi-classical theory of Eilenberger, which accounts for the temperature dependence of the superheating field.

Summary of Research:
Superconductors are an essential component of modern accelerators, used both as magnets to bend the path of the particles and as resonance cavities to accelerate them. While the former are pushed to their limits in the type-II regime where magnetic flux lines penetrate and are pinned to impurities, the latter must change the sign of the induced electric field in gigahertz synchrony with the electron packets. The time-varying electric-fields induce magnetic fields which must not penetrate the superconductor; otherwise their motion would dissipate large amounts of heat and quench the superconductivity.

Thermodynamically, it is energetically favorable for magnetic fields to penetrate the superconductor for fields larger than that Hc (for type-I materials) or Hc1 (for type-II materials).

Figure 1, left: The value of the anomalous Green’s function at a point somewhat inside the superconductor at the operating temperature of niobium (assuming a spherical Fermi surface). The angular variation shown required a few thousand Gauss points over the Fermi surface to be accurate to within 1%.

Figure 2, right: Calculated values of the superheating field at operating temperature versus the Ginzburg-Landau parameter. The black cross corresponds to the value of niobium. The calculated superheating field is about 7% larger than the corresponding prediction from Ginzburg-Landau theory.
However, in practice, there is an energy barrier to the penetration of magnetic flux at the superconducting surface, allowing for the operation of accelerating cavities with fields much larger than either $H_{c}$ or $H_{c1}$. In this regime, the superconductor operates in a meta-stable, superheated state. In principle, this state can persist with magnetic fields up to the so-called superheating field at which point the energy barrier vanishes and magnetic flux enters the material. The superheating field therefore represents a fundamental limit in the operation of superconducting accelerator cavities.

Calculating the superheating field is a linear stability problem complicated by a pre-existing spatial in homogeneity in the superconducting order parameter and vector potential. Previous estimates of the superheating field have been made within the relatively simple Ginzburg-Landau theory [1]. However, the predictions of Ginzburg-Landau theory are quantitatively only accurate for temperature very near the critical temperature. Niobium, the most common material used in cavity construction, has a critical temperature of about 9 K. In contrast, the cavities are operated at about 2 K, in a regime where the Ginzburg-Landau theory requires significant corrections. These temperature dependent corrections have been calculated using Eilenberger theory in the limit of large Ginzburg-Landau parameter [2]; however, these calculations also have limited applicability since niobium has a Ginzburg-Landau parameter of about one. The current work goes beyond previous results by using the Eilenberger formalism –involving self-consistent solutions with anomalous Greens functions, Matsubara frequencies, and integrals over the Fermi surface, to calculate the temperature dependence of the superheating field over a wide range of Ginzburg-Landau parameters and temperatures.

In addition to the added complexity of the Eilenberger formalism, the present calculation is numerically challenging due to the necessity of including a large number of Matsubara frequencies and Gauss points on the Fermi surface to obtain reasonable convergence, as shown in Figure 1. Fortunately, solving the Eilenberger equations for the anomalous Greens functions at different Matsubara frequencies and Fermi surface points is trivially parallelized. For solutions near the operating temperature, we found it necessary to solve the equations at several thousand Fermi surface points for about ten values of the Matsubara frequencies. To complete the linear stability calculation, it is also necessary to calculate the sensitivity of these solutions to infinitesimal fluctuations in both the superconducting order parameter and vector potential. In all, this process required the solution of over two million independent differential equations at each iteration of the search. By distributing this problem over tens of cores at the CNF computing cluster, we were able to obtain solutions within a few weeks for a single value of the temperature and Ginzburg-Landau parameter.

We repeat the calculation for several values of the temperature and Ginzburg-Landau parameter. Some preliminary results are given in Figure 2 for several values of the Ginzburg-Landau parameter at the operating temperature of niobium. Although the results agree qualitatively with those of Ginzburg-Landau theory, we find that the predictions of Eilenberger theory are about 7% higher for niobium at operating temperature.

The Eilenberger formalism opens the possibility of even more precise predictions about the superheating field. In particular, it is also possible to account for anisotropy in the Fermi surface and for impurities in the niobium, both of which could be significant corrections. It may also be possible predict the dependence of the superconducting gap on the induced magnetic field, a quantity important for measuring the quality of a superconducting cavity. Each of these calculations could be performed with the numerical framework developed here.

References:
Fabrication of Nanoscale Silicon Fracture Test Specimens and Calculation of Ideal Strength of Silicon

CNF Project Number: 1982-11
Principal Investigator: Alan Zehnder
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Web Site: https://confluence.cornell.edu/display/frac/Strength+of+Nanoscale+Systems

Abstract:
This work is an extension of that performed by Alan, et al. [1, 2], investigating the effect of surface characteristics on the strength of nanoscale silicon (Si) structures. Progress, utilizing CNF, during the 2011/2012 year has been focused in two main areas. We have replicated the process of Alan, et al., to fabricate nanoscale Si beams with current equipment and techniques, and have made progress in modeling Si fracture at the atomic scale using molecular dynamics. The molecular dynamics calculations have been completed using CNF’s Nanolab computing cluster.

Summary of Research, Test Specimen Fabrication:
Alan, et al., developed a method to fabricate nanoscale Si beam structures based on work by Wang, et al. [3]. We spent a large amount of effort during 2011/2012 to update Alan’s procedure with new equipment and techniques. Samples are fabricated from <111>-oriented Si wafers.

The fabrication involves two sets of photolithography and reactive ion etching (RIE) steps. The first etch depth is done to a depth of about 200 nm and roughly controls the thickness of the final beam structure. Before the next round of lithography and etching, a 100 nm thermal oxide layer is grown. The second RIE step is done to a much greater depth of about 10 µm and forms the trench above which the final beam structure will be suspended. At this point the beam is still connected to the substrate along its entire bottom side. Before removing the Si from under the beam, the devices are cleaned with a modified RCA process [4]. The beams are then anisotropically etched using KOH and tetramethyl ammonium hydroxide (TMAH). This etch terminates on Si {111} surfaces. Because the bottom side of the beams are <111>-oriented, and the top and sides are protected by the thermal oxide, the beams themselves are not etched away. Finally, the thermal oxide is removed with a buffered oxide solution. The resulting beam structure is shown in Figure 1.

Failure on Si \{111\} planes under mixed loading using molecular dynamics: Work has also been done on calculating the strength of Si \{111\} planes under mixed mode loading conditions. This is being done using the molecular dynamics code Large Atomistic and Molecular Massively Parallel Simulator (LAMMPS) and the modified embedded atom method (MEAM). Roundy and Cohen have calculate the theoretical strength of Si \{111\} planes under pure tension and pure shear in a \(<112>\) direction using density functional theory [5]. Because the top and bottom of the nanobeam shown in Figure 1 are \(<111>\)-oriented, the \{111\} fracture planes are not orthogonal to the long axis of the beam. Even though the middle of the beam is under approximately pure tensile loading at fracture, the \{111\} planes are under a mix of tensile loading as well as shear in both directions. For this reason, the Roundy and Cohen results cannot be directly compared to fracture data obtained from such beams.

Figure 1: Nanoscale Si fracture test specimen fabricated at CNF.
Thus far, the MEAM calculations have successfully reproduced the failure behavior reported by Roundy and Cohen for the pure tension and pure shear cases. The stress-strain behavior for the pure shear case is shown in Figure 2. MEAM calculates a stress and strain at failure of 35 GPa and 17% in tension, and 9.25 GPa and 28% in shear. Roundy and Cohen report 22 GPa and 17% in tension, and 6.8 GPa and 30% in shear [5]. The failure strains produced by MEAM agree with the results of Roundy and Cohen. The failure stresses are higher in the MEAM calculations because Roundy and Cohen allow all strains in the plane of the {111} fracture surface to relax. The periodic boundary conditions of the MEAM calculation do not allow for this relaxation, and thus a higher stress is required to reach the strain at which failure occurs. Work is currently in progress to extend these results to mixed mode loading cases.

References:


Figure 2: Stress-strain data calculated using MEAM for an infinite and idea Si crystal.
Bismuth Electrodeposition on GaAs <110>

CNF Project Number: 2036-11  
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Users: Xin Huang¹,², Manuel Plaza¹,², J. Y. Peter Ko¹,²  

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Abstract:  
We evaporate Au₈₈Ge₁₂/Au on GaAs wafers at the Cornell NanoScale Science and Technology Facility (CNF) to fabricate an ohmic contact on the back side of GaAs wafers.

Summary of Research:  
We use in situ x-ray diffraction to characterize the structural evolution of the thin-film during electrochemical deposition.

In order to use GaAs <110> as an electrode for electrochemical reactions, we need to fabricate an ohmic contact on the back side of the wafers. To achieve this, we evaporate an Au₈₈Ge₁₂/Au bilayer. First, we thermally evaporate 80 nm of Au₈₈Ge₁₂ eutectic alloy at a rate of 0.1 nm/s at 10⁻⁶ Torr. Immediately after, we deposit 200 nm of Au at 0.1 nm/s at 10⁻⁶ Torr by e-beam evaporation. After that, we anneal the GaAs wafers at 380° in Ar/H₂ atmosphere for 90 seconds.

In Figure 1, we show a schematic representation of the final GaAs/Au₈₈Ge₁₂/Au structure.
Origin of the Strain Sensitivity of Superconducting Triniobium-Tin

CNF Project Number: 2053-11
Principal Investigator and User: Matthias G.T. Mentink

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Primary Source of Research Funding: Lawrence Berkeley National Laboratory, under Department of Energy contract nr DE-AC02-05CH11231
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Abstract:
The effect of axial strain on the electron DOS and phonon DOS of Nb₃Sn is investigated, in order to explain the origin of the strong effect of strain on the superconducting properties of Nb₃Sn.

Introduction:
The superconductor niobium-tin or triniobium-tin (Nb₃Sn) is a widely used “workhorse” superconductor for high magnetic field applications, such as the Iter fusion project [1]. Due to thermal contraction differences and Lorentz forces, the superconductor is exposed to considerable deformation during operation. The superconducting properties of Nb₃Sn are quite sensitive to strain, impacting the performance of applications using this superconductor [2].

As Nb₃Sn is a low temperature superconductor, the circumstances leading to formation of the superconducting state are fairly well understood. In particular, the critical temperature is related to the electron density of states at the Fermi level and the phonon density of states [3], which implies that strain either affects the electron DOS, or the phonon DOS, or both.

Progress:
DFT calculations are performed using Quantum Espresso [4]. Structural optimizations are performed on a deformed cell, after which the electron DOS at Fermi level and the phonon DOS is calculated. Preliminary electron DOS results indicate a large change in electron DOS with strain (see Figure 1). Furthermore, a calculated phonon spectrum is compared to a measurement and found to be quantitatively consistent (see Figure 2).

Outlook:
Looking forward, emphasis will be placed on calculating the phonon DOS at various strain states. Using the calculation results, the strain sensitivity of the superconducting properties of the material will be calculated and compared to experimental results.

A brief overview of this work with the CNF computing facility was giving in a DOE review poster session as part as a general overview of my Ph.D. research.

Summary of Research:
The calculation results indicate that the electron DOS at Fermi level of Nb₃Sn as strongly affected by strain. The effect of strain on the phonon DOS of Nb₃Sn is ongoing, but preliminary results are quantitatively consistent with experimental data.

References:
Figure 1: Electron DOS as function of strain along <100> direction.

Figure 2: Calculated phonon DOS (at -1.5% axial compression) in light grey versus measured phonon DOS in black [5].
Mass Production of Patterned Nanowires via Electroplate-and-Lift Lithography

CNF Project Number: 2079-11
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Abstract:

Electroplate and Lift (E&L) Lithography [1-4] has been developed as fast, simple, scalable technique for the controlled, solution-based, electrochemical synthesis of patterned metallic and semiconducting nanowires. E&L lithography is the only known process that allows patterned nanowires to be mass-produced, without requiring any additional vacuum or cleanroom processing after the initial fabrication of the patterned template. The present work aims to automate both the electroplating and the liftoff steps through roll-to-roll processing. Patterned templates with over two million features have been produced, which should enable the production of nanowires at a rate of approximately four hours per gram.

Summary of Research:

An overview of the E&L lithography process is shown in Figure 1 [1]. E&L employs a reusable, non-sacrificial, multi-layered, lithographically patterned ultrananocrystalline diamond (UNCD)™ template for electrodeposition. The electrodeposition itself may be performed from either an aqueous or ionic liquid solution. To date, micro- or nanowires composed of 26 distinct elemental metals, alloys, compound semiconductors, and even conductive polymers have been deposited [2]. Following electrodeposition, the nanowires may be removed by mechanically lifting them away from the template with scotch tape or other adhesive polymers, thus regenerating the template surface for subsequent depositions. Wires of the same or a different diameter, composed of any desired electrochemically depositable material, may be electroplated.

As is diagrammed in Figure 2 [3, 4], the classic E&L template is made from alternating layers of intrinsic UNCD, which is insulating, and nitrogen-incorporated UNCD (N-UNCD), which has nearly metallic conductivity. The diamond layers are lithographically patterned and etched in oxygen plasma to expose only edges of the N-UNCD layer, which is 80 nm thick. Intrinsic UNCD is used to isolate the top and bottom surfaces of the N-UNCD layer from the electrochemical bath, thereby confining the initial nucleation of the nanowire to the patterned edges of the N-UNCD. The thickness of the conductive N-UNCD layer establishes the minimum achievable wire diameter. The maximum wire diameter is determined by the deposition time, independent of feature sizes in the template [3]. In alloy systems such as copper-tin bronze, the composition of the wires may be controlled through control of the composition of the solution [4].
Unlike all other known methods of patterning nanowires, E&L lithography allows patterned nanowires to be inexpensively mass-produced, without requiring any additional vacuum or clean room processing after the initial fabrication of the template. Although at present the setup of each electrodeposition bath and the wire removal are both performed manually, it is easy to envision the automation of both the electroplating and the liftoff steps through roll-to-roll processing, as depicted in Figure 3. A silicon wafer, patterned with a UNCD-based E&L template, would be attached to the wheel on the left, and rotated through the electrochemical bath. The wheel on the right would be coated with an adhesive polymer, to remove the newly produced nanowires and regenerate the template. This pickup wheel would rotate through a rinse bath, where wires would either be removed from the wheel by sonication, or transferred to a final collection spool coated with an even stronger adhesive.

This nanowire mass production instrument may be operated in either of two modes, interchangeable simply by changing the template. For the mass production of patterned nanowires, one may use a wafer with millions of patterned features arranged in a ring, as shown in Figure 4. This prototype template was made from a mask of ~ two million flashes. Assuming all lateral dimensions and spacings are greater than 2 µm, a 100 mm wafer can typically accommodate 1-5 million patterned features within the deposition ring. The rate of nanowire production with the template in Figure 4 is calculated to be approximately one gram every four hours. Gram quantities of shaped nanowires may have many applications, such as use in RFID taggants, control of viscosity in polymeric and colloidal materials, and the development of self-sharpening tools. Alternately, if the template pattern were a continuous circle, with its circumference positioned to coincide with the deposition ring in Figure 4, the single edge could be used to produce a continuous wire with a diameter between 100 nm and 1 µm, at a rate of approximately one kilometer per day. If made of a thermoelectric material such as bismuth, a nanowire with this ~ 109:1 aspect ratio should provide unambiguous experimental evidence related to a theoretical prediction by Dresselhaus, et al. [5], that thermoelectric materials which are nanoscale in one dimension and macroscopic in another are expected to display an enhanced Seebeck Effect.

References:
Disappearance Mechanisms of Sub-100 nm Diameter Aluminum Dots on Sapphire during Annealing

CNF Project Number: 2089-11
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Abstract:
It has been observed by the authors that aluminum nano-dots on single-crystal sapphire substrates will disappear entirely when annealed between 450°C and 1200°C, provided they are ~ 100 nm in diameter or smaller. Such dots have been fabricated at the CNF by electron-beam lithography and liftoff of thermally evaporated metal for a series of annealing experiments to identify the mechanism(s) responsible.

Motivation:
A novel and cost-effective technique for improving the efficiency of compound semiconductor devices built on sapphire substrates has been developed [1] and patented [2] at Lehigh University. This technique requires the fabrication of large arrays of nanoscale “dots” on the substrate in order to improve the quality of the grown semiconductor, leading to substantial gains in final device efficiency. To avoid the hazards inherent in fabricating nanostructures in oxides, we have made use of an annealing process for converting metallic aluminum films on single-crystal epitaxially polished sapphire substrates into sapphire that is epitaxially commensurate with the original substrate [3]. Applied to pre-existing metal nanostructures, the result is the same. Little is known about the behavior of nanoscale aluminum objects under the combined conditions of size scale, temperature range, and chemical environment which are required for the conversion process, as these conditions are extreme as compared to those typical of integrated circuit aluminum conductor structures.

We have regularly observed that during the conversion process, metal dots smaller than a certain threshold diameter (~100 nm) tend to either dramatically deform or disappear entirely during the high-temperature step of 24 hours at 1200°C, yet all dots remain unchanged after the first step of 450°C for 24h. A systematic study of aluminum nanodots annealed in the 450°C to 1300°C range was deemed necessary in order to identify the mechanism responsible for this disappearance and to determine an appropriate technique to prevent such failures in the future. The knowledge obtained in this experiment will also prove instrumental in refining the times and temperatures used in the conversion process, which had been arrived at empirically and originally tailored for use with blanket films as opposed to isolated nanostructures.

Experimental Summary:
The suspected mechanisms for material transport in the relevant temperate range are evaporation, surface diffusion, fracture at the metal/oxide interface leading to wholesale removal of the dot, or extrusion through cracks or flaws in the native oxide shell. It is possible to use the distinct temperature ranges at which each of these mechanisms are expected to be active as a diagnostic tool. In January of 2012, we used the electron-beam lithography capabilities at the CNF to fabricate suitable arrays of aluminum nano-dots for such a study. Dots in the 50-200 nm diameter range were formed by exposure of poly-methymethacrylate on sapphire (JEOL JBX-9300FS) and subsequent deposition and liftoff of 100 nm of thermally evaporated aluminum (CHA thermal evaporator). These dots were then transported to Lehigh University for characterization by scanning electron microscopy (Hitachi 4300 SEM) at normal incidence and 45° tilt, annealing, and re-characterization post-anneal.

At the time of writing, the following conditions have so far been studied: (A) 700°C for one hour, (B) 900°C for one and (C) 12 hours, (D) 1000°C for one hour, and (E) 1200°C for one and (F) 24 hours (six samples total).

Dots of all sizes remain present, even if deformed, for all of the temperatures tested below 1000°C. Complete disappearance of dots has only been observed for diameters less than 70 nm for samples (D) and (E), and in dots 80 nm or smaller for sample (F). Spreading (“slumping”) of dots of all sizes is indicated by increased diameter and changed shape at temperatures above 1000°C, and to a smaller degree in sample (C). Slumping in sample (F) is severe, leading to almost complete disappearance of dots up to 100 nm in diameter and nearly 50% increases in diameter. Hillocking...
and extrusion is seen at 900°C and below for dots larger than ~ 100 nm. Faceting is observed at 1000°C and higher, and is universally hexagonal and commensurate with the c-plane orientation of the substrate.

These results are all in agreement with preliminary observations made in the course of previous work.

**Interpretation of Results:**

The temperature threshold for disappearance at ~ 1000°C suggests that metal evaporation alone is not the mechanism responsible. The rate of metal evaporation at 900°C [4] would lead to removal of the entire volume of a 100 nm diameter dot in several minutes. Cross-sectional transmission electron microscopy of selected samples will be performed to determine at which point the dots have fully converted to oxide. Further experimentation with annealing temperatures and times and modeling based on these results is ongoing in order to conclusively determine which of the remaining mechanisms are responsible for dot disappearance. Quantitative study of dot spreading rates may also prove useful in separate studies of metal/oxide wetting and/or oxide surface diffusion.

**References:**


**Figure 1:** SEM of high aspect ratio as-fabricated aluminum dots, ~ 70-80 nm diameter, at 45° tilt.

**Figure 2:** SEM of dots in Figure 1 annealed at 1200°C for one hour. Dots are spheroidized, but remain present. Smaller diameter dots have disappeared entirely.

**Figure 3:** SEM of as-fabricated aluminum dots, ~ 130 nm diameter, at 45° tilt.

**Figure 4:** SEM of dots in Figure 3 after 1200°C for one hour, exhibiting slumping and faceting.