**Star Resist Roughness**

**CNF Project # 386-90**

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**Abstract:**
Linear and star-shaped ArF photoresists were prepared, and lithographic comparisons were performed. An oligo-initiator, based on saccharose, forms the core of the star shaped photoresist, from which three standard ArF photoresist monomers, \( \alpha \)-gamma butyrolactone methacrylate (GBLMA), methyl adamantyl methacrylate (MAMA) and hydroxyl adamantyl methacrylate (HAMA) were polymerized. Conditions were adjusted to obtain a low polydispersity, 6 kg/mol star polymer with a degree of polymerization of approximately five mers per arm. For comparison, a linear photoresist control was prepared using the same scheme. The star resist architecture was found to improve roughness without reducing sensitivity or resolution.

**Introduction:**
Improving the roughness of resist sidewalls, quantitatively measured as line width roughness (LWR) and line edge roughness (LER), without sacrificing sensitivity or resolution is a key requirement for next generation photoresists [1]. Redesigning resist architecture offers intriguing possibilities to improve the performance of photoresists, which have traditionally been linear polymers [2]. The star polymer architecture is especially interesting, although it has not been studied as a chemically amplified resist. Star polymers, while chemically identical to their linear polymer counterparts, exhibit more compact size than linear polymers of the same molecular weight [3]. This suggests that less roughness will be introduced to the sidewall during the development step if a star resist is substituted for a linear resist.

**Experimental:**
Polymerization was carried out using a procedure that will be elaborated upon in a future publication. An aliquot was removed at the start of polymerization. \(^1\)H-NMR analysis of this sample and additional aliquots taken during polymerization were compared by integrating vinyl peaks corresponding to the monomers’ vinyl groups and calibrated to anisol.

The star polymer was polymerized for 30 minutes, leading to a conversion of 44% and a composition of 50% GBLMA, 30% MAMA and 20% HAMA. The linear polymer was polymerized for 150 min, resulting in a conversion of 40% and a composition of 47% GBLMA, 35% MAMA and 18% HAMA. After purification, gel permeation chromatography was used to determine polydispersity and molecular weight. The polydispersity of both the linear and star polymer was found to be 1.16. The number average molecular weight (M) was 7.3 kg/mol for the linear polymer. Due to radius of gyration differences between the linear calibration and the star polymer, M is underestimated for the star polymer with a value of 6.3 kg/mol.

**Results and Discussion:**
Comparing the lithographic properties of resists is difficult because lithographic performance varies greatly with processing conditions. Although the samples have the same composition, different processing conditions are required to optimize the lithographic performance of each photoresist. A thermal gradient was constructed by connecting a cold and hot reservoir with a thermally conductive stage. An infrared thermometer was used to characterize the linear thermal gradient once equilibrium was reached. The photoresist samples were spin-coated onto a silicon wafer and a post-apply bake (PAB) was carried out using this stage. The samples were exposed at CNF using a JBX-9300FS electron beam to place test patterns at 20 different doses in a two millimeter square, repeated every 5 mm across the length and width of the wafer. A post-exposure bake (PEB) was carried out at a 90° angle from the PAB to create a combinatorial wafer with three processing gradients. Using a scanning electron microscope, roughness and blur was measured for each processing condition; a subset is reported in Figure 1. Processing conditions for the star resist that closely matched the sensitivity and blur of the linear resist were selected for a final roughness comparison. This was accomplished by
baking the star resist at a lower temperature than the linear resist. Under these conditions both resists exhibit similar blurring at the same doses. The resists therefore exhibit the same potential sensitivity and roughness. The mean roughness of both resists are compared at each dose (Figure 2). At every dose, the star resist demonstrates reduced roughness over the analogous linear resist. At many of these doses, the improvement is 10% or more. (Figures 3, 4) This corresponds to a one year roughness improvement on the International Technology Roadmap for Semiconductors [1].

**Conclusion:**

Sub-5 nm roughness is achieved with the star resist. This corresponds to an improvement of 12% over the equivalent linear resist without any loss to sensitivity or resolution. This suggests that star resists may perform fundamentally better than their linear counterparts. More generally, it is evidence that, although most photoresists have traditionally been linear polymers, linear polymers do not necessarily give the best performance. Additional research into alternative resist architectures, including star resists, has the potential to yield resists that can surpass linear resists.

**References:**

Abstract:
In order to meet the growing demands of the semiconductor industry, resolution limits of photoresists are being driven towards sub-30 nm patterns through the use of 193 nm and next-generation extreme ultraviolet (EUV) lithography. In order to achieve these goals, radical new photoresist designs and processes must be considered. Molecular glasses (MGs) have been modified to include photoacid generating substituents in order to limit the acid diffusion from exposed to unexposed areas. The lithographic performance of these new molecules has been compared to MGs blended with a standard photoacid generator (PAG).

Summary of Research:
Molecular glasses (MGs), a low molecular weight amorphous material, have shown promise as photoresists for high resolution lithography. As feature sizes are pushed to sub-30 nm, issues of pattern size versus molecular size arise. Traditional resists are usually composed of polymers, which can have a radius of gyration of up to 5 nm. MGs, with a size of 1-2 nm, have the potential to outperform polymeric resists when feature sizes reach the size of polymers [1,2]. However, much work needs to be done to fully take advantage of these MG resists. These molecules, equipped with acid-labile protecting groups such as tert-butoxycarbonyl (t-BOC), are mixed with a PAG, which generates acid upon UV exposure. Once the acid is produced, a post-exposure bake (PEB) step is required to initiate acid catalyzed deprotection, which renders the molecules in the exposed regions soluble in a developing solvent.

One problem still plaguing photoresists in general is acid diffusion from exposed areas to unexposed areas during the PEB step, creating line edge roughness (LER) and line width roughness (LWR). LER and LWR can have a detrimental effect on achieving high resolution patterns. A way to overcome this issue is by tethering the PAG to a MG core, thereby anchoring the PAG in the film to avoid significant diffusion [3].

PAG-attached MGs have been synthesized and their lithographic properties have been tested. Figure 1 shows the structures of the MGs with acid labile groups and PAG-attached molecular glasses. The t-BOC protected MG was blended with the PAG-attached MG in a 1:1 PAG-attached:t-BOC protected and dissolved in PGMEA to make a 5 wt% solution. The solution was spin-coated onto a bare silicon wafer at 2000 rpm for 1 min, then baked at 115°C for 1 min. The film was then exposed with an ABM contact aligner (254 nm) and subject to a PEB of 85°C for 1 minute, and subsequently developed in 0.033 N tetramethylammonium hydroxide (TMAH) for 1 min.

Figure 2 shows the images obtained after patterning 1:1 T-bound:t-BOC protected. A dose of 24 mJ/cm² was used to achieve significant contrast between the exposed and unexposed areas. A diluted sample of AZ 300 MIF (0.26N TMAH) was used as a developer because of the low protection ratio of the t-BOC protected MG. Because of the relatively large number of free hydroxyl substituents on the protected molecule, the concentration of base in AZ 300 MIF is too high for the protected molecule to be completely insoluble. Therefore, a diluted developer will still clear the exposed portions but leave the unexposed portions.
In order to test the sensitivity of the PAG-attached molecules vs. traditional PAG-blended molecules, contrast curves were created using the ABM contact aligner at 254 nm. For the PAG-blended control, a standard PAG, triphenylsulfonium perfluoro-1-butanesulfonate, was blended with the t-BOC protected MG at a concentration of 5% with respect to the resist. The contrast curves obtained are shown in Figure 3. The PAG-blended molecule showed a sensitivity of 8 mJ/cm² while the T-bound PAG attached molecule exhibited a sensitivity of about 4 mJ/cm². Since the PAG loading can be increased with the PAG-attached molecules without the adverse effect of uncontrollable acid diffusion, the sensitivity can be increased.

The PAG-attached MGs have shown promise in improving the lithographic performance of MG photoresists. Further studies include testing high resolution patterning with e-beam lithography, and ultimately EUV lithography. Analysis of LER in high resolution patterns will be carried out, as well as acid diffusion studies to confirm the large size of the PAG-attached MGs is inhibiting their mobility in photoresist films.

References:
Abstract:
We present a non-chemically amplified, acid-stable imaging material for patterning organic electronic devices. The highly fluorinated resist can be patterned at 248 nm and 365 nm conditions, and shows 100 nm resolution under e-beam exposure. We also show sub-micron patterning of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), a highly acidic material for which our photoresist is particularly suitable. Finally, we demonstrate a bottom-contact transistor patterned with our new photoresist which shows better performance than previously achieved by other patterning methods.

Summary of Research:
Organic electronics has received enormous attention as a technology platform enabling flexible, large-scale devices, by exploiting solution-processable organic materials [1]. However, for this vision to be realized, several challenges must be overcome, particularly with regard to patterning. Patterning of electronic materials allows construction of microscale device architectures for organic light-emitting displays and thin-film transistors. In spite of the proven technical advantages, conventional photolithography is not recognized as a suitable method for patterning organic materials as there can be significant deterioration of active materials upon exposure to process solvents for photolithography [2]. By introducing a set of benign processes (Orthogonal Patterning) including tailored fluorinated photopolymers and fluorous solvents, we have demonstrated that this problem can be circumvented [3].

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is a mechanically flexible, transparent, and highly conductive polymer blend, which has found various applications in organic electronics [4]. However, photolithographic patterning of PEDOT:PSS is not straightforward, because: i) PEDOT:PSS films are damaged by aqueous alkaline solutions, which are standard developers in conventional photolithography, and ii) acid-sensitive photoresists are adversely affected by the acidic nature of the PEDOT:PSS film. This challenge, however, gave opportunity to our Orthogonal Patterning, which utilizes chemically non-damaging hydrofluorooethers (HFES) for pattern development instead of aggressive aqueous solutions.

Figure 1: Non-chemically amplified photoresist processable in HFES.

In designing a photoresist for acidic PEDOT:PSS patterning, a copolymer P(FDMA-NBMA) was chosen. The highly fluorinated perfluorodecyl methacrylate (FDMA) gives the polymer solubility in HFES, and the photo-labile comonomer 2-nitrobenzyl methacrylate (NBMA) changes the solubility of the polymer films upon UV exposure (Figure 1) [5]. It should be emphasized that the photosensitive monomer NBMA was carefully selected to enable non-chemically amplified patterning; an imaging mechanism which does not rely on acid-catalyzed deprotection reactions [6]. The advantages of this pathway are substantial. Typically, following patterning with a chemically amplified resist, a thin layer (ca. 10-20 nm) of decomposed photoresist is left on the PEDOT:PSS interface due to the unwanted acid-catalyzed deprotection reactions [7,8], but our method doesn’t have this drawback.
To demonstrate patterning properties, P(FDMA-NBMA) was lithographically evaluated on both Si and glass substrates. The resist polymer was spin-coated from HFE-7600 and then patterned under 248 and 365 nm UV light. Pattern development was carried out in HFE-7200.

Figure 2 shows well-resolved sub-micron lines on Si. At 248 nm, the dose is 84 mJ cm$^{-2}$ whereas at 365 nm, the dose is 2700 mJ cm$^{-2}$. The photoresist was also patterned under electron-beam (ebeam) exposure conditions. Well-resolved lines down to 100 nm were obtained.

P(FDMA-NBMA) was then used to demonstrate patterning of PEDOT:PSS films. P(FDMA-NBMA) films were spun-cast on top of the PEDOT:PSS layer and then patterned at 365 nm. Pattern resolution was consistent with that of the photoresist patterned on Si alone. Patterns were transferred to PEDOT:PSS via O$_2$ plasma etching and the photoresist was subsequently removed. PEDOT:PSS patterns with sub-micron resolution were obtained (Figure 3).

To demonstrate the potential of this resist, we fabricated simple bottom-contact organic transistors (OTFTs) with patterned pentacene films on top of patterned PEDOT:PSS source and drain electrodes. The optical image and atomic force microscopy (AFM) images of a typical 5 µm channel length OTFT device are shown in Figure 4. OTFTs with channel lengths of 5, 10, 20, and 50 µm were fabricated and tested. The value of 0.03 cm$^2$ V$^{-1}$s$^{-1}$ was obtained for the charge carrier mobility in the saturation regime. The on-off current ratio was found to be more than $10^4$. The obtained values for carrier mobility are higher or comparable to previously reported values for pentacene channel, PEDOT:PSS electrode OTFTs achieved by other patterning techniques.

References:
Abstract:

The chemical waste generated in today’s microelectronic fabrication processes has driven the need to develop a more environmentally benign process. Silicone fluids are linear methyl siloxanes that are non-toxic, not ozone-depleting and can be easily recycled. They are used as environmentally friendly alternatives in this study to develop conventional photoresists. After silylation, two conventional photoresists, poly(hydroxystyrene-co-t-butylacrylate (ESCAP) and poly(4-t-butoxycarbonyloxystyrene) (PBOCST) have been successfully developed in silicone fluids, with features as small as 100 nm.

Summary of Research:

The use of chemical solvents in the developing processes of photoresists can result in gross waste production [1,2]. The chemical waste generated is not only costly to treat but also harmful to the environment. In addition, most of these chemicals could release into the environment and raise concerns about environmental, health, and safety hazards. Therefore, many solvents have been proposed as environmentally friendly alternatives for developing photoresists. In this report, we used silicone fluids as environmentally friendly developers to process photoresists. Silicone fluids, also known as linear methyl siloxanes, are a class of mild non-polar solvents with low molecular weights, which contain only silicon, carbon, hydrogen, and oxygen. The chemical structure of one of the silicone fluids, decamethyltetrasiloxane, is shown in Figure 1. They are low in toxicity, contribute little to global warming, do not contribute to ozone depletion [3]. They do not accumulate in the atmosphere, but are rapidly transformed to naturally occurring chemical species and can be recycled. Because of their advantageous chemical and physical properties, they have been used as components of cosmetic and personal formulation [3]. They have also been used for water removal in microelectronics processing, lubricating and cleaning applications [4]. The solvent strength of siloxanes is weaker than that of saturated hydrocarbons but stronger than that of the commercially available saturated hydrofluorocarbons and may be enhanced by adding other solvents [4]. Besides their environmental friendliness, silicone solvents have low surface tension, which has the potential to eliminate pattern collapse in high aspect-ratio features.

Two conventional photoresists, poly(hydroxystyrene-co-t-butylacrylate (ESCAP) and poly(4-t-butoxycarbonyloxystyrene) (PBOCST) are used in this study, with their structures shown in Figure 1. Both photoresists were insoluble in silicone fluids before and after exposure. However, we were able to enhance the dissolution of the resists in silicone fluids by using (N,N-dimethyl) trimethylsilane (DMTS) as a silylating agent. The structure of DMTS is shown in Figure 1. Lithographic evaluation of both photoresists was done by using the CNF’s GCA Autostep 200 DSW i-line wafer stepper and JEOL 9300 electron beam lithography system, and their Tencor P10
profilometer was used to measure the film thickness before and after development in silicone fluids. It was found that DMTS was able to react with the hydroxyl groups in unexposed ESCAP and exposed PBOCST and form trimethylsilyl groups which increase the solubility of unexposed ESCAP and exposed PBOCST in silicone fluids. By using DMTS, we were able to develop both ESCAP and PBOCST in silicone fluids. Scanning electron microscopy (SEM) images of ESCAP and PBOCST developed in decamethyltetrasiloxane are shown in Figure 2 and Figure 3, respectively.

By using (N,N-dimethyl)trimethylsilane and silicone fluids, we were able to develop negative-tone image of ESCAP and positive-tone image of PBOCST, and features as small as 100 nm were obtained.

In conclusion, we have shown a novel and environmentally friendly process to develop photoresists in silicone fluids. Silicone fluids are not only environmentally benign but also have the potential to eliminate problems like pattern collapse, and we have shown promising results of using silicone fluids to develop conventional photoresists with features as small 100 nm.

References:
Abstract:
Natural processes of molecular self-assembly between two dissimilar polymer chains are combined with chemically amplified photolithography in order to achieve pattern formation at two length scales. The block copolymers formed consist of a crosslinkable negative-tone photoresist and a degradable block in order to generate nanoporous thin films. Here we discuss new techniques within block copolymer lithography, which can be used to transfer sub-20 nm features into silicon substrates as a tool for next-generation patterning.

Summary of Research:
As traditionally chemically amplified photoresist technology approaches its theoretical limits, new material innovations are required in order to extend lithographic patterning below the 20 nm critical dimension. Block copolymer self-assembly is one of the techniques under consideration to extend the range of high-resolution patterning into the molecular realm. Block copolymers are two polymers connected in series by a covalent bond. The formation of mesoscopic features (10-100 nm) are in essence a thermodynamic phenomena. They are a consequence of a balance in enthalpic and entropic forces: the repulsion force opposing the mixing of the two polymer chains and the force of chain elasticity, which pulls the chains back into a randomly coiled configuration. The manipulation of a few variables, such as molecular weight, volume fraction, and the degree of incompatibility between the blocks, allows sufficient control over the size and shape of functional polymer units. By incorporating a negative-tone photoresist as one of the blocks of the block copolymer to crosslink the matrix, and having the other block selectively removable, our group has shown the ability to form nanoporous “stencils” that can be used to resist the dry or wet etching processes used in traditional lithography [1]. We are currently exploring two different platforms for block copolymer self-assembly, which are suitable for both 254 nm and 193 nm top-down lithographic patterning, respectively.

The first system under consideration is poly(α-methylstyrene-block-4-hydroxystyrene) (PαMS-b-PHOST), in which the negative-tone photoresist PHOST is used for 248 nm top-down patterning, and the PαMS block can be removed via dry etching techniques to create a nanoporous thin film. Previous work in the group has shown the ability to reversibly switch the morphology from spheres to cylinders through a solvent vapor processing technique, in addition to the ability to “lock-in” these morphologies through the crosslinking of the PHOST matrix phase in conjunction with photoactive compounds [2,3].

Recent work on this system has focused on the addition of new functionality into the block copolymer matrix, including hafnium-oxide based nanoparticles (Hf-NPs) of 2-3 nm diameter. 60% of the weight of the Hf-NP consists of condensed inorganic hafnium, while the balance consists of an organic ligand which is used to enthalpically interact with the PHOST block through hydrogen bonding interactions.
Figure 1 shows a TEM image of a PαMS-β-PHOST block copolymer bulk film with a periodic lamellar morphology and microdomain repeat spacing equal to 25 nm. The PHOST phase appears dark through the incorporation of 30 wt.% Hf-NP (relative to the weight of the PHOST block) after physically mixing the block copolymer and Hf-NP in an organic solvent and drying.

If this blend is spin-coated as a thin film, the high inorganic content in Hf-NP increases the oxygen plasma etch durability of PHOST dramatically, becoming greater than that of the PαMS block at above 30 wt.% Hf-NP, as shown in Figure 2. However, above 50 wt.% Hf-NP, we observe macrophase separation of the Hf-NP out of the PHOST host polymer (not shown), indicating a fundamental limit in the amount of inorganic that can be incorporated into the hydrophilic block. Regardless, the disparate etching behavior of the two blocks in this nanocomposite material could be used to efficiently transfer the self-assembled pattern into a silicon wafer. Additionally, the refractive index (RI) of PHOST+40% Hf-NP was measured as approximately 1.6 at 632.8 nm using the Woollam variable angle spectroscopic ellipsometer at the Cornell NanoScale Facility. After the removal of the PαMS phase, the large RI difference between air (RI = 1) and the PHOST-Hf-NP block could allow for the creation of a self-assembled waveguide structure.

Figure 2: The oxygen plasma etch resistance gained by incorporation of hafnium-oxide nanoparticles into a PHOST homopolymer becomes greater than that of the poly(α-methyl-styrene) block above approximately 30 wt.% Hf-NP loading.

The system under study, tailored for 193 nm lithography, is poly(2-hydroxyethyl methacrylate)-block-poly (methyl-methacrylate) (PHEMA-b-PMMA). In this block copolymer system, the PHEMA block is used as a negative tone photoresist and has a low absorbance at 193 nm, allowing for lithographic patterning at this wavelength. The PMMA block can be removed using a 248 nm flood exposure followed by development in acetic acid. With the addition of small amounts of photoacid generator (1.5 wt.% triphenylsulphonium triflate (TPST)) and a cross-linker (4 wt.% tetramethoxymethylglycouril, (TMMGU)), films of crosslinked PHEMA-b-PMMA were spincoated, followed by UV exposure and development in THF.

Figure 3 shows a scanning electron microscope (SEM) image that shows the generated lithographic patterns with resolution down to 1.2 µm scale using a contact mask aligner system. Higher resolution would be expected with the use of lower wavelength (193 nm) patterning technique.

References:
Low Heat Capacity Substrates for Calorimetry Measurements

CNF Project # 522-94
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Abstract:
This project focuses on synthesis and characterization of material systems, which are constrained to small dimensions. One goal is to develop thermal analysis methods and instruments such as nanocalorimetry to probe nanometer scale particles of metals, polymers and nanoliter volumes of proteins [1]. Special sensor devices needed for nanocalorimetry can be fabricated using CNF micromachining [2] capabilities. A variety of interesting materials phenomenon occur only at the nanometer length and have been investigated, such as the size-dependence melting point depression and magic number sizes in metal nanoparticles [3], order-disorder transitions of self-assembled monolayers of alkanethiols (SAMS) [4], and thickness dependence of glass transition in polymers [5]. In this report, we discuss our work on the synthesis and characterization of thin films and nanometer-size clusters of Ag with alkanethiol that form large multilayer silver-alkanethiolate (AgSR) crystals [6].

Summary of Research:
Metal-thiolate complexes (metal = Au, Ag, Cu, etc.) are currently of growing technological and scientific interest. The transition of metal-alkanethiolate to nanoparticles upon electron beam irradiation makes it a potential material for electron beam writing. Recent studies also demonstrated the luminescent properties of metal-thiolate complexes. Luminescence of metal complexes has long been a research interest for applications in photoactive reagent, light-emitting diode, and sensors for volatile organic compounds.
Metal-thiolate complexes are also important in the liquid-phase synthesis of metallic nanoparticles as it is considered to be an intermediate product in the reaction sequence. Metal-thiolate complexes, monolayer protected clusters (MPCs), and self-assembled monolayers (SAMs) on extended metal surfaces are the three major species in the binary system composed of metal and thiolate. One of the key differences among them is the S/metal ratio. Among the metal-thiolate complexes, the polycrystalline polymeric silver alkanethiolate (AgSR, R = C(n) - H(2n + 1) prepared in liquid-phase synthesis has been characterized.
AgSR has a planar polymeric structure with a -Ag-S-network as the central plane (backbone). Fully extended alkyl chains are bonded to S extending on both sides and are perpendicular to the central plane. The arrangement of the alkyl chains in AgSR is analogous to that in two dimensional (2D) SAMs on planar substrate. However, the overall composition ratio of S/Ag and the synthesis method are much different for these two kinds of alkanethiolates. AgSR has the ratio of S/Ag = 1.0, and can be produced by using Ag salts and alkanethiol. In contrast, 2D SAMs are obtained by immersing a bulk solid (planar Ag substrate) into an alkanethiol solution, and the effective overall composition approaches zero (S/Ag = 0) since only the Ag surface reacts with alkanethiol to form alkanethiolate. This reaction is self-limiting.

We developed [6] a new synthesis method in which both AgSR and MPCs coexist as reaction products. The new method employs the reaction of alkanethiol with nanometer-sized Ag islands on inert substrates: low-residual-stress silicon nitride (SiNx). This method is similar to the preparation of 2D SAMs on planar substrate, except that the exposed Ag islands have highly curved surfaces. The effect of the curvature weakens the self-limiting effect allowing for the formation and coexistence of both MPCs and AgSR. Nanocalorimetry is especially useful for this study since it is designed for thin-film samples.

We characterize and compare the reaction of alkanethiol with Ag continuous planar thin films and Ag islands on inert substrates. During thermal annealing, ripening occurs that generates large AgSR lamellae having diameters of 1 micron and thickness up to 30 layers. Nanocalorimetry data (Figures 1 and 2) shows Cp of both the 2D SAMs systems and the 3D MPC with AgSC16 lamella samples. Atomic force microscopy data (Figures 1 and 3) show the single-
layer step-heights of individual crystals, which match the layer thickness obtained via x-ray diffraction analysis. The crystals have facets and flat terraces with extended area, and have a strong preferred orientation (001) normal to the substrate surface.

References:

Abstract:
We report the direct patterning of multi-component polymer brush systems: patterned block copolymer brushes and patterned binary brushes. By direct e-beam patterning of positive-tone/negative-tone block copolymer brushes, micro- and nano-channels were successfully created. Direct patterning of positive-tone/positive-tone block copolymer brushes was also carried out, and their phase separation was found to be influenced by the pattern size. By direct patterning and sequential re-growth, we also prepared patterned binary brushes. The binary brushes showed interesting responsiveness to solvent.

Summary of Research:
Polymer brushes can be formed by densely attaching polymer chains to a substrate. Due to the covalent grafted chains and their stretched conformations, they show special bulk and solution properties. Recently, patterned polymer brushes have attracted great interest because of their potential applications in microelectronics, templated synthesis, anti-fouling, and biosensing. Conventional patterning methods for polymer brushes require multiple-step initiator patterning followed by grafting-from polymerizations, which has the risk of causing more contaminations [1,2]. Conventional patterning also causes low resolution of the patterns due to the relaxation of the polymer chains during the polymerization process [3]. Previously, our group has developed a new strategy to directly pattern the polymer brushes by electron beam (e-beam) lithography. Several types of polymethacrylate brushes were first grown from initiator-immobilized substrates via atom transfer radical polymerizations (ATRP), and then directly patterned by e-beam lithography [4,5]. Sub-50 nm high resolution patterns of the homopolymer brushes were successfully achieved.

We have extended the direct patterning method to the patterning of multi-component polymer brushes, namely, block copolymer brushes and binary brushes. It is well known that under e-beam exposure, positive-tone polymer resists for e-beam lithography undergo chain scission reactions, while negative-tone resists crosslink. We have prepared block copolymer brushes with poly(methyl methacrylate) (PMMA) as the bottom block, and polystyrene (PS) as the top block. PMMA is a common positive-tone e-beam resist, while PS is a negative-tone resist. Under e-beam exposure, the PMMA chains are scissioned and the PS chains are crosslinked. After development, micro- and nano-channels are formed. These channels could potentially be used for microfluidics and templated synthesis of inorganic nanomaterials.

We also patterned dual-positive-tone block copolymer brushes by direct e-beam lithography. Poly(2-hydroxyethyl methacrylate) (PHEMA) is also a positive-tone resist. Block copolymer brushes with PHEMA as the top layer and PMMA as the bottom layer were prepared and
directly patterned. Due to their incompatibility and phase separation, the patterned block copolymer brushes show different morphologies in their patterns. It is found that the arrangement of the morphologies is influenced by the pattern size and solvent treatment. Figure 1 shows a typical atomic force microscope image of the patterned PMMA-\textit{b}-PHEMA brushes.

By direct patterning and sequential re-growth, we are also able to prepare patterned binary brushes. PMMA brushes were first patterned by e-beam lithography, and the ATRP initiators were then re-immobilized to the patterned area. By regrowth of poly(oligoethylene glycol methyl ether methacrylate) (POEGMA), amphiphilic binary PMMA/POEGMA brushes were prepared. These brushes show their responsiveness to good and bad solvent. The corresponding brush component can swell significantly in its good solvent, and can cover the collapsed neighboring brushes.

The direct patterning method has shown its robustness in preparing patterned multi-component polymer brushes. These brushes may show special properties, and are currently under further investigation.

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References:
Abstract:

We fabricate large arrays of highly-crystalline, single-domain nano-islands of the ferroelectric polymer PVDF. Thin films of the polymer are patterned using nano-imprint lithography and characterized using an atomic force microscopy (AFM) in piezo-response force (PFM) mode. The resulting structures form a low-loss, nonlinear dielectric suitable for microwave devices in flexible electronics.

Description:

The novel impulse-radio architecture recently developed in our group shows strong potential for short-range, low-power wireless communications [1,2], however its performance is limited by substrate losses in complementary metal oxide semiconductor (CMOS). The advantages of this architecture are best realized in a material system such as flexible electronics, where transistors are relatively slow, but passives (inductors and capacitors) have high quality factors. Implementing such a radio requires high-quality voltage-variable capacitors to be fabricated with a thermal budget less than 200°C to avoid damaging the substrate.

Our target material is the ferroelectric polymer, polyvinylidene fluoride (PVDF), which behaves as a nonlinear dielectric up to optical frequencies, but has strong losses in the 10 MHz-1 GHz range due to dielectric relaxation. However, these relaxation processes have been associated with the amorphous regions and amorphous-crystalline boundaries which exist in a continuous thin-film [3,4]. Therefore, the ability to fabricate fully-crystalline, single-domain PVDF should enable high-frequency applications in flexible electronics.

In this project, we attempt to fabricate and characterize metal-insulator-metal capacitors using large area arrays of single-domain PVDF islands as the dielectric. The islands are patterned using nano-imprint lithography, Figure 1, where a template is pressed into a PVDF thin film under heat and pressure sufficient for plastic deformation of the polymer. The template consists 20 nm lines and 100-200 nm spaces over a large area and is created by e-beam.
lithography (JEOL 9300) with an HSQ negative resist. The template can then pattern several PVDF films in the NX-2500 nano-imprint tool. Figure 2 shows part of a large array of islands on silicon. Figure 3 shows a partially successful imprint onto gold/chrome metal.

Initial characterization of the islands (before deposition of the top metal layer) uses an AFM technique called Piezoresponse force microscopy (PFM) to measure the PVDF’s electro-mechanical response. (Because the ferroelectric effect also induces piezoelectricity in PVDF, the electro-mechanical and dielectric responses correspond closely.) PFM applies an AC voltage to the AFM tip and monitors the magnitude and phase of the cantilever deflection to measure the piezoelectric displacement and domain orientation, respectively. Figure 4 shows a PFM phase image of individually-poled PVDF islands; the PFM measurements are performed on the Icon AFM, as well as CCMR’s Dimension 3100 AFM.

The ability to polarize individual PVDF islands suggests that highly-crystalline, low-loss material has been formed. Future process development will complete metal-insulator-metal capacitors and allow microwave frequency electrical measurements and implementation of impulse radio devices.

References:
Abstract:
We have developed a new method to induce preferential alignment in organic thin films of a highly anisotropic small molecule, pentacene. Growth on pre-patterned substrates results in grain nucleation along a lithographically defined pattern. This improvement in morphology control and grain registration in organic thin films allows further investigation of transport across grain boundaries and within single grains.

Summary of Research:
Organic electronics is an emerging technology with promises of low-cost and large-area processing and fabrication of organic thin film transistors and photovoltaics on flexible substrates [1]. With recent development of lithographic patterning methods for organic materials [2], our research focus has shifted to controlling the morphology and achieving grain-scale registration in organic thin films. Preferential alignment of organic films on a substrate is an important step in achieving high crystallinity and high performance of organic thin film transistors, where high crystallinity is not sufficient for high performance due to strong anisotropy in most organic materials. Therefore, registration between grain orientations and contact electrodes becomes an important criterion in device performance.

An early attempt to achieve preferential alignment of organic films was demonstrated with anatomically stepped silicon substrate [3]. In this case, pentacene grains nucleated and grew along the silicon step edges. This process produced large pentacene grains demonstrating a preferential crystallographic alignment to the silicon step edges. Unfortunately, the underlying silicon substrate is impractical for organic electronics applications.

In our work we developed an alternative and more robust method of creating step-edged substrate by patterning self assembled monolayers (SAMs) using photolithography. By utilizing SAMs, we are able to tune the step height and step edge energy through the length and chemical composition of the SAMs. The step edge density is controlled by photolithography. This process also allows us to use a wider range of substrates.

Currently, we are working with a single layer step edge model shown in Figure 1. This system inhibits the formation of large grains spanning multiple step edges due...
to impingement of differently oriented grains produced by neighboring steps. Using this model we have grown pentacene films on substrate with 3 µm patterned lines of HMDS and 3 µm unpatterned lines of SiO₂. Produced thin films demonstrate preferential nucleation of pentacene grains along the step edges (Figure 2), as expected from the model. Therefore we are able to achieve preferential nucleation of pentacene grains along the patterned step edges leading to an improved registration between pentacene grains and electrodes upon further patterning. These films are now being used to investigate transport across grain boundaries and within single grains.

References:

Figure 2, right: a) AFM image of pentacene grown on a SiO₂ substrate patterned by 3 µm HMDS vertical lines separated by 3 µm. b) Average height profiles along the horizontal and vertical directions. Height profiles show grain spacing of 3 µm along the horizontal direction, corresponding to the spacing between the pre-patterned step edges.
Abstract:

We aim to investigate the 1/f noise of MgO-based magnetic tunnel junctions (MTJs) with high tunnel magnetoresistance (MR) and the influence of processing on the 1/f noise. The stack structures used are Ta 5/ Cu 20/Ta 3/IrMn 10/CoFeB x/MgO 1.2/CoFeB x/Ta 8/Ru 7 (thickness in nanometers and x is either 3 nm or 50 nm). The junctions are patterned into micro-sized sensors (Φ50-200 µm circles). The MgO junctions have a MTJ about 120% after annealing at 380°C. Noise measurement is in progress to study the effect of the CoFeB thickness and the annealing process on the 1/f noise.

Summary of Research:

The development of small (sub-millimeter), inexpensive (a few tens-of-dollars each), low-frequency (0.01 Hz to 100 Hz), ultra-sensitive (nT or pT range), low-power (a few milliWatts or less) magnetic sensors has been under intensive research due to their wide possible applications in medical, military, information technology and industrial communities [1,2]. Magnetic tunnel junctions (MTJs) are a promising candidate for such sensors thanks to their intrinsic high resistivity and low power consumption, high magnetoresistance (MR), small dimensions, thermal robustness, room-temperature operation, radiation resistance, and fast response [3]. More recently, important progress has been made in the aspect of MTJ fabrication with the discovery of MgO-based MTJ in 2004 [4,5], which makes the understanding of the origin of noise and investigating its correlation with the design parameters and processing more important than ever before any serious success is achieved for the applications as ultra-sensitive magnetic sensors.

The MTJ in this work comprises two ferromagnetic CoFeB layers separated by an insulating MgO layer. One of the CoFeB layer is pinned by coupling with an adjacent antiferromagnetic IrMn layer using the so-called exchange anisotropy phenomenon, and the other one is the free layer. Minor loop corresponds to the reversal of the free CoFeB layer. Figure 1 shows the typical minor loops of magnetoresistance of samples having structure CoFeB 3 nm / MgO 1.2 nm / CoFeB 3 nm at room temperature. The MR curves of Figure 1 exhibit a very sharp rise corresponding to the switching of the free layer as the external field increases. Additionally, the minor loops are centered at 10 Oe, have a coercivity of around 20 Oe. The 10 Oe loop shift of the nominally free CoFeB layers indicates the presence of a slight ferromagnetic coupling by the pinned layer through the insulating MgO layer. As shown in Figure 1, annealing at 380°C in Ar atmosphere increases the MR from around 22% to 120%, which allows the realization of very high MR sensitivity at low fields.
Figure 2 and 3 show the bias voltage ($V_{bias}$) dependence of MR and output voltage of different MTJs. As shown in the figures, the MR of all MTJs is observed to decrease and the output voltage, which is defined as $V_{bias} \times MR$, exhibits a maximum with increasing values of applied voltage. Research suggested that this universal bias dependence was intrinsic and possible causes include: the creation of magnons, variation of the density of states in the ferromagnet with applied voltage, and decrease in the tunnel barrier height with voltage [6]. According to Figure 3, the operating $V_{bias}$ should be around 250 mV to get a high $V_{out}$.

For magnetic sensors, the noise performance indexed by the signal-to-noise ratio (SNT) is particularly important. It is known that low frequency noise of MTJs is dominated by 1/f noise, though other noise sources including shot and Johnson noise, amplifier noise, thermal magnetic noise may also play a role. Noise measurement is in progress to understand the origin of noise and investigate its correlation with the design parameters and processing.

References:
Abstract:
Most microfluidic applications are channel-based, where flow networks and valves need to be designed, fabricated and placed on the chip \textit{a priori}, and reconfiguration of flow networks cannot be done on-the-fly. Since flow paths are fixed, it is difficult to change the analysis performed based on earlier results, and manufacture versatile chips for diverse applications. Here we describe an opto-thermal technique to trigger reversible structural changes within a microfluidic device thus enabling large scale reconfiguration of microscale environments on the order of seconds. Channel networks and valves can thus be dynamically created and reconfigured on-the-fly by dynamic photomasking.

Summary of Research:
Previous work on optical reconfiguration of microfluidic flow has either required the use of high power lasers, and/or high switching times [1, 2]. Our technique offers a fast and low power approach to create and reconfigure channel and valve structures \textit{in situ}. As shown in Figure 1, this effect uses two coupled processes; (1) Photothermal conversion, where energy from an optical image is converted into a local thermal field using an absorbing substrate, and (2) Thermorheological conversion, where the thermal field triggers a reversible change in the rheology of a polymer solution flowing within the microfluidic device, resulting in the creation of local regions of high yield strength that behave as wall-like structures.

We have used this technique to demonstrate both flow valving and channel reconfiguration. The polymer solution used here is an aqueous solution (14.5 - 15\% w/w) of Pluronic F127 (BASF, USA), a triblock copolymer consisting of poly(ethylene oxide)$_{106}$—poly(propylene oxide)$_{70}$—poly(ethylene oxide)$_{106}$. This aqueous solution undergoes a sol-gel transition at about 30°C.

Figure 1: Schematic demonstrating opto-thermorheological flow manipulation.

Experiments - Flow Valving:
Reconfigurable valve elements were created using a microfluidic chip with an absorbing substrate consisting of either indium tin oxide (ITO) or sputtered gold [3]. Figure 2 shows an experiment demonstrating the creation of reconfigurable valve elements. Light from a low power laser (405 nm, 40 mW) was used to illuminate one of the arms of a bifurcating channel through a 20x objective. The absorbing substrate served to convert the optical energy from the laser to thermal energy, thus locally heating the thermorheological solution flowing through that channel. This local heating resulted in a sol-gel transition, and the
subsequent increase in viscosity caused the flow through that arm of the channel to be valved and diverted to the other channel. No such valving took place for the control case of a plain glass substrate which has poor absorption at 405 nm.

**Experiments - Channel Reconfiguration:**

Here, using a standard projector system fitted with a focusing lens to project images onto a chip, we demonstrate the creation and reconfiguration of entire channel structures. The substrate of the chip consists of a glass slide coated with poly(dimethylsiloxane) or PDMS, followed by a thin layer of carbon black and PDMS, which acts as the absorbing layer. Figure 3 shows an experiment where channels are configured on-the-fly within a microfluidic chamber. A narrow straight channel running through the center of the chip is created within a larger microfluidic chamber. The time scale of channel creation and reconfiguration is on the order of seconds. On turning the optical field off, the original flow field is recreated, demonstrating the reversibility of this technique.

**Fabrication:**

The microfluidic chamber used for our experiments was fabricated using photolithography techniques and was made with PDMS. The fluid layer was formed by first making a mold on a silicon wafer by deep silicon etching using the Unaxis 770 Bosch Etcher. Sylgard 184 silicone elastomer base and curing agent were mixed in a ratio of 5:1 to make the PDMS used here. PDMS was poured over this mold and cured to fabricate a microfluidic chamber having a height of 25-50 µm.

The substrates used in the case of the flow valving experiments consisted of plain glass, sputtered gold and ITO coated substrates. The plain glass and ITO substrates were bought and used as is, while the sputtered gold substrate was fabricated by using the SEM sample preparation sputtering system to sputter a thin layer of gold on a plain glass slide. The PDMS layer was bonded to the glass substrate by plasma cleaning both layers, aligning and leaving them overnight in a convection oven at 80°C. It was bonded to the other substrates using a thin layer of spun curing agent on the substrate to serve as an adhesion layer, followed by an overnight baking step in a convection oven at 80°C.

The substrates used in the experiments for channel reconfiguration consisted of glass slides with a thin layer of PDMS (5:1) to improve the heat transfer characteristics of the device. The absorbing layer was formed by mixing carbon black (Cabot Corp, USA) with PDMS and pouring the resulting mixture onto the PDMS coated glass substrate. After dessicating and baking the above substrate in a convection oven at 80°C for two hours, the microfluidic layer was bonded to the substrate using a technique similar to that described for the PDMS-glass bonding above.

**References:**


Abstract:

We preliminarily report the structural and electrical properties of Bi-V-O thin film library using 90° off-axis RF sputtering and high-throughput analysis technique [1,2]. Continuous compositional spreads (CCS) was able to represent 1000 different compositions in a material library at a time. X-ray diffraction, Raman spectroscopic studies revealed the structural variation as a function of sample geometry and composition. Some of the electrical characterization such as dielectric constant, and polarization hysteresis were performed, and revealed the unknown complex oxide phase and well-known perovskite phase [3]. Our novel CCS approach will open the possibility for investigation of new complex oxides system.

Summary of Research:

Before depositing complex oxide thin films library, we prepared a thermally grown 200 nm SiO₂ layer by using wet oxidation of a 3 inch Si wafer after MOS cleaning. To fabricate 100 nm for the Pt bottom electrode, we used 20 nm of a TiO₂ buffer layer as a sticky and diffusion barrier by using CVC sputtering system, then the Pt bottom electrode was grown by either e-beam evaporation or sputtering. For the CCS oxide thin film library, 90° off-axis RF magnetron sputtering was optimized at various oxygen partial pressures and substrate temperatures utilizing a Bi and V metal target co-sputtering method. For electrical characterization, a Pt top electrode was deposited by using 100 µm diameter of shadow mask, resulting in a metal-insulator-metal configuration to measure capacitance, polarization, and current-voltage characteristics. Surface morphology observed by SEM and crystalline phase was identified by x-ray diffraction.

Figure 1 shows a schematic compositional variation and linear capacitance mapping of Bi-V-O complex oxide thin film library as a function of sample position. A distinct higher capacitance region in both of the Bi-rich (region b) and the V-rich (region c and d) side was obtained.

There were optically white bands between region b and c, which were always formed in every deposition process, even with different oxygen partial pressures and substrate temperatures. It seemed to be a higher surface energy area on this white band region. Unfortunately, electrical measurements could not be taken, and the crystal structure was not identified in this region.

Various grain morphologies at a certain region from a-e were observed, and are shown in Figure 2. The region of the Bi-rich phase (a-b region) showed a triangular shaped grain, while the V-rich region presented rod like grains (region d) and large irregular grains (region e), which were composed of a number of sub-grain features inside. In addition, the middle point (region c) showed polygonal shaped
characteristics. This specific surface morphology could have originated as a compositional gradient as a function of the sample position.

The crystalline phase of the complex oxide Bi-V-O thin film was obtained in the a-e region as shown in Figure 3. In accordance with the morphology and capacitance variation, we could observe distinct phase evolution; regiona a and b were indexed as Bi$_2$O$_3$-like phase, while c-e regions could be indexed as a complex Bi$_x$V$_y$O$_z$ phase with a V$_2$O$_5$, VO$_2$ combination. Full mapping and phase identification of the crystal structure on every point will be performed in high energy x-ray diffraction method using the synchrotron source at the Cornell High-Energy Synchrotron Source [4].

Sawyer-Tower measurements were performed, putting the P-E hysteresis at a frequency of input voltage above 1 kHz, which was represented in Figure 4. A linear dielectric response was observed in the Bi-rich region (a and b), and some in the V-rich Bi-V-O complex region (c and d) showed non-linear dielectric response (polarization hysteresis). Even though a circuit modification was required to detect a leaky ferroelectric region, we will extract the quantitative polarization value in the near future.

However, it should be noted that a higher capacitance region coincided with the ferroelectric hysteresis region, which was responsible for the ionic vibration mode in the anti-symmetric crystallographic orientation. Thus it is required, at a later time, to investigate vibration mode mapping utilizing Raman spectroscopy or FT-IR spectroscopy.

References:
Design and Property of Directional Self-Cleaning Superoleophobic Surfaces

CNF Project # 1614-07
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Abstract:

Functional surfaces with self-cleaning property are highly desirable in many applications in the printing industry. In this study, we report the creation of textured surfaces on silicon (Si) wafers—by photolithography, followed by chemical modification—that are superoleophobic and exhibit directional self-cleaning property. The textured surfaces are made of micro grooves, which demonstrate interesting anisotropic wetting behavior. In the direction parallel to the grooves, low surface tension testing liquids show very low sliding angle (i.e. directional self-cleaning) which is a key enabler for the self-cleaning effect.

Summary of Research:

Over the recent decades, inspired by nature and motivated by its amazing self-cleaning effect on Lotus leaves, researchers have created superhydrophobic surfaces by various approaches [1]. These efforts usually involve the combination of surface roughness and surface chemistry. However, most man-made contaminants are organic in nature, a high degree of oleophobicity is needed. More specifically surfaces with superoleophobicity are a lot more valuable and practical than surfaces with superhydrophobicity alone [2]. All the Xerox imaging materials are organic matters with low surface tension and we are interested in studying the interactions of superoleophobic surfaces with various imaging materials with the aim of improving future print processes and printing systems.

Fabrication and Surface Property of a Directional Self-cleaning Superoleophobic Surface on Si-Wafer:
The superoleophobic model surface is fabricated by first creating the textured silicon (Si) surface on a Si wafer by photolithography, followed by molecular vapor deposition (MVD) of a fluorosilane, tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) [3] on the textured surface. Both static contact angle and dynamic contact angle measurements of water, hexadecane, and the Xerox wax ink (at elevated temperature) were performed on a goniometer model OCA20 from Dataphysics.

Figure 1 shows a scanning electron microscopy (SEM) micrograph of a textured surface with groove structure, consisting of ~ 3 mm diameter pillars, ~ 6 µm in pitch, and ~ 4 mm in height on Si wafer. Figure 2 shows the detailed wavy structure of the side wall created by the Bosch etching process. The re-entrant structure at the top of the groove structure is geometrically critical to achieving surface superoleophobicity [2,3].
Anisotropic wettings are obtained on this textured groove structure (Figure 3). The water contact angles are at 131.3° and 153.8° when measured from the parallel and the orthogonal directions of the groove, respectively. The water contact angle for a comparable pillar structure was ~ 156° [3]. For hexadecane (HD), contact angles on the groove structure are 113.2° and 161.8° from the parallel and the orthogonal directions as compared ~ 158° on pillar structure [3]. Similarly, the contact angles for the Xerox wax ink at elevated temperature are at 119.7° and 156.3° in the direction of parallel and orthogonal to the groove structure, respectively. The results indicate that the groove structure is both superoleophobic and superhydrophobic in the orthogonal direction. The surface properties are identical to the comparable pillar structure. Both oleophobicity and hydrophobicity reduce somewhat in the parallel direction.

Sliding angles for 10 mL of water and hexadecane droplets (7.5° and 4.1°, respectively) are small, even smaller than the pillar structure, in the parallel direction. This is despite of the smaller static contact angles in the parallel direction. The sliding behavior depends on where the contact line is located and how the drops move (sliding off or rolling off). A continuous short contact line may be preferable for a surface where droplets are sliding off; while a discontinuous and irregular contact line could be better for a surface where droplets are literally rolling off. The contact angle hysteresis is consistent with sliding angle results.

**Evidence for the Cassie-Baxter State:** Two states are commonly used to describe the liquid-solid interface on rough surfaces: the Cassie-Baxter state and the Wenzel state. The static contact angles for a droplet at the Cassie-Baxter state (θ_{cb}) and the Wenzel state (θ_{w}) are described in [4,5].

The re-entrant structure, shown in Figure 2, maintains the low surface tension liquids, including the molten ink in the Cassie state. This means that the testing liquids “sit” on a composite surface consisting of mostly air and a solid with significantly decreased contact area. This also prevents the low surface tension liquids from entering the Wenzel state (wetting state: liquid fills up the grooves on the rough surface, characterized by high contact angle, large hysteresis and high sliding angle or pinned). Although contact angles for both states are significantly increased for both states, the Cassie state is desirable due to its low sliding angle and low adhesion between the ink and textured surface.

The liquid-solid interface has been directly studied by putting the Xerox molten wax ink on the textured superoleophobic surface in a heated chamber and carefully taking off the ink drop when it solidifies at room temperature. An SEM of the interface is given in Figure 4. The result clearly shows that the ink drop does penetrate into the groove (~ 1 µm), but never touches the bottom (~ 4 µm height). This observation is consistent with its high contact angle and low sliding angle, suggesting that the testing liquid drops are in the Cassie-Baxter state and primarily “sits” on air in the groove structure.

**References:**


**Figure 3:** Anisotropic wetting on the textured groove structure from parallel (left) to orthogonal (right) direction with water, hexadecane (HD) and the Xerox wax ink.

**Figure 4:** SEM of the solidified wax ink-substrate interface showing little penetration of the molten ink into the groove valley.
Electronic Structure of Semiconductors and Molecular Magnets

**CNF Project # 1666-08**

**Principal Investigator(s): Richard Hennig**

**User(s): Michael Lowe, Frank Petruzielo, Eva Smith, Arunima Singh**

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**Summary of Research:**

**Frank Petruzielo:** Molecular calculations in quantum Monte Carlo frequently employ a mixed basis consisting of contracted and primitive Gaussian functions. While standard basis sets of varying size and accuracy are available in the literature, we demonstrate that reoptimizing the primitive function exponents within quantum Monte Carlo yields more compact basis sets for a given accuracy. Particularly large gains are achieved for highly excited states.

For calculations requiring non-diverging pseudopotentials, we introduce Gauss-Slater basis functions that behave as Gaussians at short distances and Slaters at long distances. These basis functions further improve the energy and fluctuations of the local energy for a given basis size. Gains achieved by exponent optimization and Gauss-Slater basis use are exemplified by calculations for the ground state of carbon, the lowest lying excited states of carbon with \(^1S^o\), \(^3P^o\), \(^1D^o\), \(^3F^o\) symmetries, carbon dimer, and naphthalene. Basis size reduction enables quantum Monte Carlo treatment of larger molecules at high accuracy [1].

**Michael Lowe:** Our research on Nanolab consists of three main projects. The first two consist of predicting properties of species involved in lithium-sulfur batteries, and the third project was a quick structural analysis of a novel nitride. Lithium-sulfur batteries have the highest theoretical energy density of any secondary battery system, but implementation is limited due to a complex discharge mechanism. We are using Gaussian03 to predict reduction potentials for a range of polysulfide species, to complement ongoing electrochemical and spectroscopic data about key polysulfides involved in battery operation. Although there are significant differences between the computational and electrochemical environment, we have demonstrated that in the cases with experimental data, the DFT-predicted reduction potentials correlate with the observed values. We are also using a finite-difference method approach to predicting spectroscopic transitions (FDMNES) to predict the x-ray absorption signal near the sulfur K-edge for select sulfur-based compounds. This modeling has enabled us to resolve some unexpected features in the x-ray absorption spectroscopy of lithium sulfide.

The third project uses DFT within the code VASP to predict the ground-state structure of some nitride/oxide compounds. The recently-synthesized AgTaN\(_2\) is the first crystal to report covalent Ag-N bonding, and the computed structure for the nitride was used to demonstrate that the reported lattice parameters and positions are reasonable and thermodynamically stable. The results have been included in a paper that will be submitted for publication soon.

**References:**

Abstract:

Catalyst features were patterned onto quartz substrates, from which well-aligned carbon nanotubes could be grown. Scanning electron microscopy was used to characterize the growths. Subsequent experiments with the carbon nanotube samples included array devices integrated into fluidic cells and on-chip Raleigh imaging and spectroscopy.

Summary of Research:

Carbon nanotubes (CNTs) have garnered much attention over the last two decades for their interesting and sometimes novel properties, which hold promise for a number of diverse applications [1]. An exciting recent synthetic development has been the capability to grow long, highly-aligned CNTs [2,3]. We have been using CNF resources to help prepare samples for aligned CNT growth and for characterization afterward.

Photolithographically-defined mapping marks are first etched into a quartz wafer, which is then diced into small chips. After an overnight anneal, lines of iron catalyst, 10 µm wide and spaced 150 µm apart, are patterned onto the chips. Using a chemical vapour deposition (CVD) furnace in our lab, we can grow well aligned CNTs, which serve as samples for further experimentation. Representative scanning electron microscope (SEM) images are provided in Figure 1.

These carbon nanotubes grown on quartz have served as initial samples for a variety of subsequent experiments. For example, electrodes have been deposited onto the quartz chips to form nanotube array devices from which fluidic cells were constructed. The cells combine bulk electrical characterization that includes electrolyte gating capabilities with an optical window, which could facilitate simultaneous spectral and electrical information to be gathered as chemicals are introduced to the cell in real time.

In another project, the as-grown samples served as a platform for on-chip Raleigh imaging and spectroscopy of carbon nanotubes. A representative optical micrograph of elastically scattered light from individual single-walled carbon nanotubes under widefield laser illumination is provided in Figure 2.

References:

Figure 1: SEM images of well-aligned CNTs grown on a quartz substrate; (a) wide view, (b) close up of catalyst line.

Figure 2: Representative spatial Rayleigh image showing more than 20 SWNTs simultaneously. Scale bar = 20 µm. [Courtesy of Daniel Joh, also in the Park Group].
Surface Modification of Polymer Substrates with Ionic Nanoparticles

Abstract:
We explore the use of nanostructured coatings based on colloidal silica as a generic route to tune and regulate the surface properties of a versatile range of synthetic polymers. Our methodology relies on Coulombic forces of attraction between the cationically modified silica nanospheres and the localized negative charges on the argon/plasma treated substrate. Those interactions give rise to multilayer coatings that impart desired functionalities to the polymer and also exhibit remarkable stability and durability.

Summary of Research:
Nanostructured coatings carry a great potential for a wide range of applications such as preparation of ultraviolet radiation resistant, anti corrosive, self cleaning, photocatalytic, antibacterial, superhydrophilic or superhydrophobic materials. As a consequence of intensive research efforts in both academia and industry, a series of nanoscopic coating formulations has recently become commercially available.

Within the course of this project, we focus on the development of a simple, yet general, deposition process using functionalized inorganic nanoparticles on argon/plasma treated polymeric substrates varying from ideally smooth all the way through to highly textured surfaces. To that end, we have recently demonstrated that our approach can render polypropylene fabric superhydrophilic [1], a result not reported so far for that polymer.

Continuing our studies in this field, we extend the investigations by considering polycarbonate as the substrate, a polymer that exhibits exceptionally enhanced physical properties such as impact resistance and clarity, rarely seen in other materials. X-ray photoelectron spectroscopy (XPS) suggests that the level of surface oxidation (as monitored by the gradual evolution of O peak shown in Figure 1) depends on both the field amplitude and exposition time [2]. As shown in Figure 2a, the water advancing contact angles of the polycarbonate substrates are significantly reduced after plasma treatment, while subsequent deposition of positively charged silica nanoparticles gives rise to further improvement in the wetting behavior. SEM imaging (Figure 2b) suggests a complete and uniform coverage of the polycarbonate substrate after a single deposition cycle (immersion of the substrate to the suspension, solvent removal and repeated rinsings in water).

The coating quality critically depends upon the following parameters; the nature of the functional groups attached to the silica surface, the zeta potential, the size of the colloidal particles and the pH of the suspension. Furthermore, the topological characteristics of the bare substrate play a key role to the final morphology of the deposited layers and, by doing so, have a great effect on the final surface properties of the coated material.

References:
Figure 1: Water advancing contact angles of plasma treated polycarbonate substrate before (squares) and after (circles) deposition of the functionalized nanoparticles, as a function of plasma exposition time. (Black line corresponds to the untreated substrate).

Figure 2a: XPS spectrum of plasma treated polycarbonate substrate after deposition of silicon nanoparticles.

Figure 2b: SEM image of the plasma treated polycarbonate substrate coated with cationically modified silica nanoparticles.
Abstract:

We seek to exploit the confinement of acoustic phonons in nanoscale dimensions to engineer the thermal transport properties of materials. To improve our understanding of such effects, we are developing a phonon spectrometer to study nanoscale heat transport. These studies will be applied to improving the efficiency of thermoelectric power generators. In this report, we discuss the design and fabrication of the spectrometer geometry and the fabrication of superconducting tunnel junctions (STJ) to be utilized as quasi-monochromatic phonon sources and detectors.

Summary of Research:

The geometry of the phonon spectrometer is such that one STJ acts as a source of phonons, while a second STJ detects those that traverse the sample. Conventional superconductors exhibit energy gaps ($2\Delta$) of order ~1 meV in their quasiparticle excitation spectrum. Biasing of the generator STJ at voltages greater than $2\Delta/e$ will populate excited states, thereby emitting phonons via relaxation and recombination across the energy gap. By controlling the bias, a narrow range of phonon frequencies may be selected. At the detector, incident phonons will be distinguished by the change they induce in the tunneling current. Such techniques will ultimately enable spectral, temporal, and spatial investigation of phonon transport, the primary means of heat transfer in semiconductors.

We have fabricated superconducting Al-AlO$_x$-Al tunnel junctions using standard stepper photolithography at CNF, followed by deposition of Al in a dedicated evaporating chamber outside of CNF. A lithography pattern appears in Figure 1.

We have tested the junctions at a temperature of 0.3°K in a helium-3 refrigerator. The design of the spectrometer geometry furthermore involves the fabrication of relief structures on a wafer substrate. To this end, we have fabricated mesa structures (~2 µm high) formed by shallow depth anisotropic KOH etching of silicon as shown in Figure 2 [1]. Using these etched structures, we plan to study phonon transport through silicon and other materials.

References:

Figure 1: Microphotograph of a lithography pattern.

Figure 2: Microphotograph of anisotropically etched silicon mesa structures.
Vertically-Aligned Carbon Nanotube Membrane for Solar Hydrogen Generation

CNF Project # 1782-09
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Abstract:
We are developing a vertically-aligned carbon nanotube (VA-CNTs) membrane for solar hydrogen production. To fabricate the membrane, we have been growing vertically-aligned carbon nanotubes on micro porous silicon with an iron catalyst using chemical vapor deposition (CVD). Following the carbon nanotube growth a polymer is deposited to fabricate the membrane [4,5].

Summary of Research:
To be able to use hydrogen as a clean and environmentally friendly source of fuel on a large scale, production of it using a clean source of energy and not fossil fuels is necessary [1]. Out of the possible energy resources, solar is the most widely available and most abundant source for long-term carbon free energy although there are still many challenges in reaching that goal [1,2]. In this project, we are developing a vertically-aligned carbon nanotube membrane that will ultimately be used to harvest solar energy and store it in the form of hydrogen.

Using p-type micro-porous silicon as a substrate and e-beam evaporated 5 nm Fe catalyst, a dense forest of vertically-aligned carbon nanotubes (VA-CNTs) was grown by a chemical vapor deposition (CVD) process, using ethylene gas at 1000 sccm as the carbon source at 700°C for 10 to 20 minutes with the samples set in a quartz boat [3]. The samples are first oxidized at 300°C open to air for 12 hours, and the chamber is then cleared with Ar and the temperature is set to 700°C before introducing the carbon source [3]. A film thickness of over 100 µm covering a 1 cm² area was achieved (Figure 1).

For fabrication of a conductive VA-CNTs membrane, a polymer (PMMA) was deposited on the VA-CNTs, spin-coated at 2500 rpm, and then set to dry at 70°C and 15 inch Hg [5].

Future work includes conductivity measurements of the VA-CNT membranes and systematic studies of the membrane integrity.

References:
The Eccentroid as a Universal Shape for Driving 3D Self-Assembly

CNF Project # 1788-09  
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Abstract:
Creating three dimensional (3D) structures with a specific architecture remains a scientific goal far from being achieved [1]. Inducing the spontaneous association of microscopic building blocks into macroscopic structures seems to be a promising way to create these new materials. Such fabrication processes require interactions between microscopic building blocks. For depletion or deoxyribonucleic acid (DNA) interaction [2,3], the attractive energy between the particles is proportional to the overlapping surface between the colloids. Controlling the positions and orientations of the microscopic building blocks is a critical issue in such processes. To address this issue, we are looking for a shape that has the ability to align in a single configuration when it interacts with a similar shape.

The Eccentroid as a Universal Shape for Driving 3D Self-Assembly

Summary of Research:
The shape must be such that the aligned configuration corresponds to the only existing minimum in the energy landscape: the shape has to be carefully chosen such that the energy landscape does not exhibit any metastable configuration. A schematic example is shown with two colloids of complex shapes in Figure 1. When the two colloids overlap, they interact and orientate in order to maximize the overlapping surface and therefore minimizing the energy. The shape chosen in Figure 1 is not a good one as we can see that configuration 1b is an obvious metastable position in which the two colloids may be trapped. This shape is a typical example of a shape we are not looking for. Preliminary studies have shown that the shapes, called eccentroids, shown in Figure 2 should automatically align. The simplest shapes we could figure out so far are simple circular disks with a hole inside. We found that the hole has to be off-center and its radius cannot exceed some critical ratio of the outer circle diameter. These shapes have only one stable point in their energy landscape, which is obtained when the inner holes are aligned.

Let’s consider the shape on the left, which simply consists of a disk with an off-centered hole in it. One can prove that two identical particles having such shapes translate and rotate to find a minimum of energy when they interact. We can qualitatively explain why such a shape works. Consider two eccentroids which are perfectly aligned and centered. We displace one center of a small distance $\varepsilon$.

Such a displacement induces a decrease in overlapping area equal to $2\pi \varepsilon R$, where $R$ is the radius of the disk. Clearly, such a change cannot for sure exceed a gain in overlapping area equal to $4\pi \varepsilon r$, where $r$ is the radius of the inner hole. This proves that the position for which the centers of the outer circles are aligned corresponds to a maximum of overlapping respective to any translation of the shapes. Proving that there is a unique minimum is however not obvious and requires some more computations. Once the centers are aligned, it is clear that the position for which the holes are perfectly aligned corresponds to a maximum of overlap and therefore to a minimum of energy.

We synthesized microscopic colloids using the equipment in Cornell NanoScale Facility (CNF) [4]. So far, by using an i-line AutoStep, we have been able to make particles of external diameter $\sim 5 \mu m$ and inner hole of radius of $2 \mu m$. On a 4” wafer, we can process of the order of $6 \times 10^7$ particles at a time.
So far we have printed the colloids on a thin layer of SU-8 (~ 400-500 nm). This is performed at the CNF. Within two days of work, 20 wafers could be prepared.

After release from their substrate, the colloids are centrifuged and washed in water with SDS. The final solution is very stable. We couldn’t obtain depletion. Particles were further characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM). SEM pictures obtained from particles before the lift off show some halos next to the edges (Figure 3). Particles seem to have rounded edges and not sharp edges, according the SEM pictures. These observations are confirmed by using AFM and environmental SEM on eccentroids after the lift-off process. We found that the particles have small spots on their surface and that there are some very rough peaks just next to the edges of the particles (Figure 4a and Figure 4b). We could also detect the presence of some impurities located at the surface of the particles (see white spots on the SEM pictures). Another interesting fact is that the size of the hole seems to be much smaller than the size measured by SEM or optical microscope.

We have found a shape which should be able to uniquely determine the orientation and the positions of colloids in 3D. We have shown that the shape would work at the macroscopic scale using the capillary interaction as attractive interactions. In order to prove the generality of our finding, we want to find an equivalent illustration at the microscopic scale using the depletion interaction as an attractive interaction. So far, it looks like the colloids we are able to make have some roughness defects which are now our limitation.

References:
Abstract:

Silicon carbide (SiC) is a well known thin film material in the micro-electromechanical systems (MEMs) industry [1]. It can be deposited by many different techniques. For this research project at Cornell, we are exploring SiC thin film properties deposited on both silicon and glass wafer materials using plasma enhanced chemical vapor deposition (PECVD).

Summary:

The Ion and Plasma Equipment (IPE) Inc. PECVD system in the Cornell NanoScale Facility (CNF) was used to deposit amorphous, thin films of SiC from silane and methane source gases. The PECVD tool had not been used for SiC deposition for a very long time. So there was no information on how the various deposition parameters would affect the thin film material properties. Thus in the first months of this project, the goal was to explore some of the major deposition parameters and the resultant effects on the film properties. In general, the film stress and optical constants were consistent with the existing literature [2]. We did notice there is significant non-uniformity of the thin films in this tool, as shown in the Filmetrics area plot in Figure 1. The film thickness varies by more than a factor of two across the wafer. Nevertheless, in small areas, it will meet the needs of this proprietary research project.

References:
