Monolayer-Mediated Patterning of Electroceramic Thin Films
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I. Abstract

Integrated electroceramic thin film devices on semiconductor and insulator substrates feature a variety of attractive attributes, including high capacitance density, nonvolatile memory, sensor/actuator ability, and other unique electronic and optical properties. The ability to pattern such ceramic materials atop semiconductor substrates, thus, is a critical technology. Patterned oxide thin film devices are typically formed by uniform film deposition followed by somewhat complicated post-deposition ion-beam or chemical etching in a controlled environment. We review here the development of an ambient atmosphere technique which allows selective deposition of electroceramic thin layers without such post-deposition etching. In this method, substrate surfaces are selectively functionalized with hydrophobic self-assembled monolayers to modify the adhesion of subsequently deposited solution-derived electroceramics. The selective functionalization is achieved through microcontact printing (µ-CP) of self-assembled monolayers of the chemical octadecyltrichlorosilane on substrates of technical interest. Subsequent sol-gel deposition of ceramic oxides on these functionalized substrates, followed by lift-off from the monolayer, yields high quality, patterned oxide thin layers only on the unfunctionalized regions. A variety of microrange dielectric oxide devices have been fabricated using this process, with lateral resolution as fine as 0.5μm. In this paper, we review the monolayer patterning and electrical behavior of several patterned electroceramic thin films, including Pb(Zr,Ti)O₃ [PZT], LiNbO₃, and Ta₂O₅. An applied device example is also presented in combination with selective MOCVD deposition of metal electrodes: integrated, fully monolayer-patterned Pt/PZT/Pt/Si(100) ferroelectric memory cells.

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II. Introduction

Progress in the deposition of oxide thin films has allowed integration of films as planarization layers, flat panel display electrodes, and many other device elements. The ability to pattern oxide thin films into complex structures is an area of active research, required for specific applications in electronics including use as capacitors, actuators, sensors, electrochromics, and memory cells. For these applications, the ability to rapidly pattern electroceramic films into fine scale device architectures without deleterious effects on properties is a key concern. For many materials, the process of blanket material deposition, photolithographic resist patterning, and subtractive etching is an effective patterning method. The inherent chemical stability and refractory nature of many ceramics often presents difficulty for this process, though. Subtractive patterning methods often utilize reactive ion etching (RIE) and wet chemical etching, which increase the complexity of processing since they may require controlled environments, etch anisotropically, and leave residual chemical artifacts related to SF₆, HF, HCl, or other etchant species. The capability of avoiding such methods is especially attractive for such materials as LiNbO₃, which is notoriously unetchable (Å/s etch rates) by the above methods, and for PZT, which often requires dedicated RIE equipment to avoid lead contamination. Recent work with self-assembled monolayers suggested promise for patterning the initial deposition of inorganic phases by surface functionalization of substrates, thereby avoiding etching requirements. The application of such monolayers to patterning of solution-derived electroceramic thin layers was explored accordingly.
III. Self-assembled monolayers and patterning methodologies

The capability of moderating the adhesion/adsorption of materials on surfaces is reliant on the robust, hydrophilic or hydrophobic nature of self assembled monolayers, and their ability to alter substrate surface properties. Self-assembled monolayers (SAMs) of octadecyltrichlorosilane were first reported by Sagiv in 1980, and these monolayers have since found diverse application for surface passivation (corrosion resistance), friction modification (tribology), biosensing, and nanoscale control of chemical reactions. The unusual feature of such monolayers lies in the ability to order into dense, continuous, and chemically and thermally robust layers, allowing global changes in surface character due only to formation of a typically 10-30Å self-assembled monolayer. Two common types of monolayers, alkanethiols and organosilanes, and the manner in which such monolayers self-assemble, are illustrated in Figure 1. These monolayers can be generally characterized as consisting of an anchor sulfur (alkanethiol SAMs) or silicon (organosilane SAMs) atom, an organic [-CH₂₋]ₙ chain of 6-30Å in length, and an end functional group that may be either hydrophilic or hydrophobic. A major advance in SAM preparation was the deposition of thiol SAMs from dilute solutions in simple solvents such as hexane, ethanol, or acetone, reported by Nuzzo and Allara. Spontaneous organization of these films was observed to occur while in solution, resulting in monolayer film heights of 4-21Å for theoretical molecular lengths of 6-25Å, which indicates the molecules stand near-normal to the substrate surface, fully extended. Infrared data indicated the monolayers are at full extension due to molecular packing, similar to the zigzag bonding and arrangement cartoon of Figure 1. The key finding is that self-assembled monolayers are ordered, closely packed molecular assemblies, even if not perfect compared to single crystals.

The end group of such monolayers, denoted as X in Figure 1, may be tailored to be either hydrophobic (e.g. -CH₃) or hydrophilic (e.g. -OH, -COOH), enabling control of surface reactivity by monolayer functionalization. Major advances have recently been reported by Whitesides and co-workers, Bunker et al., and Collins et al. on the ability to pattern such monolayers at the
submicron scale, achieving selective functionalization. While other methods form complete monolayers and later selectively remove regions by either ultraviolet exposure\textsuperscript{16}, or charged beams\textsuperscript{8,15}, the method of microcontact printing developed by Whitesides and co-workers\textsuperscript{7,9-14} selectively deposits monolayers by a method akin to stamping ink onto paper, but on submicron to multicentimeter scales. The method of microcontact printing\textsuperscript{7} consists of five steps: (i) ultraviolet/electron beam lithography and removal of \textasciitilde 1\,\mu m thick photoresist atop a substrate, (ii) curing of a crosslinkable polymer atop this patterned photoresist, (iii) removal of the elastomeric polymer stamp from this surface, (iv) coating of the stamp with a dilute (\textasciitilde 10mM) monolayer solution in a solvent, and (v) stamping of this solution to deposit self-assembled monolayers on substrate surfaces (Figure 2).

In our research, printed organosilane monolayers were used to modify the surface wetting and tribological interaction of substrates with solution-deposited ceramic thin films. Thiol monolayers self-assemble readily above gold substrates, while organosilanes (e.g. octadecyltrichlorosilane, an 18-chain organosilane) order on a wide variety of substrates.
IV. Electroceramic materials patterning

The protocol developed for monolayer-mediated selective deposition of solution-derived oxide thin films is illustrated in Figures 2 and 3. Stamps for this process were created by curing of polydimethylsiloxane (PDMS) over etched photoresist according to the method of Kumar and Whitesides\textsuperscript{7}, producing stamps with \footnotemark[-12] \footnotetext[-12]{A 10mM solution of octadecyltrichlorosilane (OTS) in hexane was applied to the PDMS stamp by using a photoresist spinner (3000rpm for 30s) and dried in a stream of research-purity Ar. Substrates were cleaned by deionized water, acetone, and isopropanol, and dried under a stream of Ar. The stamp was brought into contact with the substrate by hand for \footnotemark[12] \footnotetext[12]{30 sec, forming microcontact printed, self-assembled monolayer patterns.}

Sol-gel precursors for PZT\textsuperscript{17,18}, LiNbO\textsubscript{3}\textsuperscript{19-21}, and Ta\textsubscript{2}O\textsubscript{5}\textsuperscript{22} were spin coated atop such monolayer patterned substrates, which included Si, Al//Si, Pt//Ti//Si, sapphire, glass, and other materials. In a typical deposition, a patterned substrate was flooded with 200\textmu{l} of 0.3M solution precursor and spin coated at 3000rpm. After pyrolysis of organics by placing the substrate on a preheated 200°-300°C hot plate, films of 80-100nm thickness were obtained. To effect lift-off of oxide above monolayer-functionalized regions, these films were then washed with isopropanol or gently polished using a nonabrasive cloth (i.e., Metcloth, Buehler Corp.), wet with isopropanol. Following liftoff, during which film deposited atop monolayer-functionalized regions de-adhered, the patterned films were then densified and crystallized by rapid heating to 700°C. Patterning of electrooptic (LiNbO\textsubscript{3}), dielectric (Ta\textsubscript{2}O\textsubscript{5}), and switchable ferroelectric materials was readily achieved following this protocol\textsuperscript{18,21-22}. 
Monolayer-mediated selective deposition of LiNbO$_3$

As described above, microcontact printing allows submicron scale patterning of surfaces with monolayers, altering the chemical nature of such functionalized surfaces$^{7,9,14}$. Octadecyltrichlorosilane was chosen as a hydrophobic monolayer, to provide contrast with the comparatively hydrophilic surfaces of oxide and metal substrates. Functionalized substrates bore $\sim25\text{Å}$ monolayers of this siloxane after stamping, determined by ellipsometry. A $25\text{Å}$ monolayer stripe of OTS is shown in Figure 4, revealed in topography mode by atomic force microscopy. Monolayers used in this study were found to maintain their hydrophobic functionalization to 400°C, as determined by observation of surface wetting angle of water droplets prior to and after annealing of monolayer-functionalized surfaces.

The method used to deposit thin layers atop these monolayers was consistent for all solutions, and involved several steps: preparation of a dilute alkoxide precursor solution, spin coating onto OTS microcontact printed substrates, low temperature heat treatment, removal of delaminated oxide, and a final high temperature heat treatment. The results of this processing for LiNbO$_3$ on SiO$_2$/Si are shown in Figures 5a-d. Figures 5a-b show amorphous LiNbO$_3$ films deposited atop a substrate fully functionalized by the hydrophobic monolayer, except in 4\text{µm}-120\text{µm} wide strips, spaced 250\text{µm} apart. In Figure 5a, it is apparent the LiNbO$_3$ atop the bare (unfunctionalized) substrate appears dense, while the film above the remainder of the substrate appears crazed and non-uniform in appearance. After nonabrasive polishing with isopropanol, this substrate appears as in Figure 5b, with the LiNbO$_3$ only adhering to the stripes of bare substrate, and with the crazed film atop the monolayer completely removed from the monolayer-derivatized regions. In Figure 5c, an optical micrograph of a similarly patterned LiNbO$_3$/Si is shown, along with Auger electron spectroscopy compositional analysis of a horizontal line across this structure. It is readily apparent that true selective deposition has been achieved, with continuous LiNbO$_3$ film on the surface where Si is not, and no LiNbO$_3$ present on the functionalized Si, which bears no film.
In pursuit of waveguide applications, films of LiNbO$_3$ were deposited atop OTS-monolayer printed 1cm$^2$ sapphire [Al$_2$O$_3$ (00.1)] substrates. In this case, the same stripe pattern of Figure 5b was used to define ~100nm thick, 4-120nm wide, 1cm length stripe waveguides. Results of this functionalization, spin coating, 300°C heat treatment, and polishing were similar to those of Figure 5a-d. Films were then rapidly heated to 700°C to heteroepitaxially crystallize these stripe waveguides, obtaining the structures shown in Figure 6a-b. In Figure 6a, a 1cm$^2$ substrate is shown, patterned with 4-120µm wide, heteroepitaxial waveguides illuminated by uniform side lighting of the structure. In Figure 6b, a single 100nm thick, 120µm wide, >1cm length LiNbO$_3$ waveguide is shown guiding a TE$_0$ mode of an end-coupled He-Ne laser. X-ray diffraction, θ rocking curves, and TEM selected area diffraction (Figure 6c) for this structure confirmed the heteroepitaxial (00.6)LiNbO$_3$//(00.1)Al$_2$O$_3$ structure, with grains aligned to within 0.7°C of each other. The combination of integrated, epitaxial, electroceramic films with monolayer patterning enables a new array of potential applications for these materials.

**Mechanism of selective deposition: model system Ta$_2$O$_5$**

Due to the complex evolution of perovskite-type compounds, often including intermediate phase formation such as A-site carbonates, the patterning mechanism was investigated with a more simple metal oxide. Ta$_2$O$_5$ is a representative ceramic thin film material, simple in chemical structure, and of interest as a possible higher dielectric constant ($\varepsilon_r = 22$) replacement for SiO$_2$ ($\varepsilon_r = 3.9$) as gate oxide in integrated circuit devices. The microstructural evolution, stress development, and patterning reliability of Ta$_2$O$_5$ thin film microstructures were investigated to assemble a broader understanding of monolayer-mediated selective deposition of oxide thin films.

Sol-gel precursors for Ta$_2$O$_5$ were made from solutions of tantalum ethoxide [Ta(OCH$_2$CH$_3$)$_5$, 99.99%, Aldrich] in absolute ethanol, with various solution additions, as explained below. These solutions were cast by spinning onto patterned or fully OTS monolayer functionalized Si, Pt/Si, Al/Si, TiN, and other substrates using a commercial photoresist spin
coater, as described for LiNbO₃. Following low temperature (100-300°C) heat treatment and removal of delaminated oxide, the patterned films were crystallized at 700-800°C, forming crystalline, insulating dielectric thin layers. Films displayed dielectric constants from 18-25 and $\tan \delta = 0.007-0.02$ at 1kHz and 100mV, with breakdown strengths around 300kV/cm.

The results of prototypical selective deposition of Ta₂O₅ onto an aluminum-coated silicon substrate are shown in Figures 7 and 8. Solutions of tantalum ethoxide in ethanol, spin coated at 3000rpm onto an aluminized silicon wafer and heat treated to 300°C, produced selective deposition as shown in the micrographs presented in Figure 7. The darkest regions are deposited oxide above bare substrate, while the crazed regions are oxide deposited above the hydrophobic monolayer (Fig. 7a). Gentle washing in isopropanol or rubbing with a non-abrasive polishing cloth enabled "lift-off" of the oxide above the hydrophobic regions, producing the patterned film shown in Figure 7b. In addition to simple linear shapes, complex patterns of sharp detail were readily formed (Fig. 8a). Fine features as small as 4μm are readily obtained for 700Å thick layers of Ta₂O₅ (Fig. 8b), with the limiting resolution determined by the efficiency of the lift-off technique. It is noted that the film thickness appears to inversely correlate, in a qualitative manner, with the resolution achieved. Thus it was found that thinner oxide layers enabled higher resolution. This ultimately is expected to enable submicron lateral resolution for the ultrathin dielectric layers that are desired for capacitor, DRAM cell, and interlevel dielectric (ILD) applications. In the current demonstration, a worst case edge resolution of better than ±100nm for 4μm width shapes was observed, as shown in Figure 8c. The potential appears to exist for engineering surface topology to optimize edge resolution²².

Hot stage ellipsometric studies (Gaertner L116C ellipsometer) for sol-gel Ta₂O₅ thin films deposited on Si indicated that a decrease in thickness occurs coincident with the initial solvent evaporation and that a more gradual densification continues up to 500°C²². For a Ta₂O₅ film constrained in the plane but undergoing volume shrinkage, development of significant tensile stresses would be expected. These stresses appear to play a vital role in the selective deposition obtained on the functionalized substrates shown in Figures 7 and 8. Stress analyses of Ta₂O₅
layers on Si were performed with a hot stage wafer bending apparatus\textsuperscript{23-25} for two limiting cases: (i) Ta$_2$O$_5$ deposited directly on Si, and (ii) Ta$_2$O$_5$ deposited on a Si wafer bearing a monolayer of OTS across its entire surface. For the case of Ta$_2$O$_5$ deposited on unmodified Si, the stress evolution observed on heating followed what might be expected from the ellipsometry data: monotonic increases in stress occur coincidental with shrinkage and densification behavior (Figure 9a). On cooling to room temperature, these stresses decrease but still remain high - around 100 MPa. This further indicates that the stress evolution was due to constrained volume decrease during densification in addition to the thermal expansion mismatch between Ta$_2$O$_5$ and silicon. This monotonic increase in stress contrasts sharply with the stress evolution seen on functionalized surfaces. For these films (Figure 9b), the thermally-induced apparent stress decreased rapidly, falling to zero during the evaporation step. Above 200°C stresses began to develop, indicating that some modest degree of adhesion is obtained above this temperature despite the presence of the monolayer. The inset micrographs shown in Figure 9 contrast the dense, high stress Ta$_2$O$_5$ films obtained on unfunctionalized Si and the heavily fractured, delaminated, and thus low stress Ta$_2$O$_5$ films which form on monolayer-derivatized Si.

The latter data suggest that the mechanism of patterning is closely coupled to that of stress release by film de-adhesion above functionalized regions of the substrate. Similar ellipsometry, stress data, and adhesion behavior were observed for LiNbO$_3$ layers on Si\textsuperscript{20}. This de-adhesion is readily controllable by the hydrophobic monolayer over a certain temperature window (for Ta$_2$O$_5$, around 80-200°C). Below 200°C the delaminated layers remained de-adhered and were readily removed by a variety of methods, such as blowing on or rinsing of the substrate, while above 200°C the increasing mechanical adhesion to the substrate complicated removal, requiring wet, but non-abrasive polishing. This is consistent with earlier work\textsuperscript{21}, which indicated that in many cases mere washing with isopropanol removed delaminated oxide, while more severe heat treatment required gentle agitation with cotton felt to remove the weakly bonded, delaminated material. Further experiments to control the state of stress (high stress, low film thickness) have improved submicron pattern resolution down to around 0.5μm feature sizes.
Monolayer patterning of Pt//PZT//Pt//Si ferroelectric memory cells

While in many cases, device patterning of oxide material elements is the dominant complication, several other materials classes also present etching difficulty. While wet chemical etchants exist for noble metals such as silver and gold, platinum patterning typically requires reactive ion etching or imprecise lift-off techniques. As platinum is also the dominant electrode used for fabrication of integrated PZT-based ferroelectric nonvolatile random access memories (NVRAM or FERAM\textsuperscript{26}), monolayer patterning may be a natural solution to the difficulty of patterning both Pt and PZT for multilayer Pt//PZT//Pt//Si FERAM device architectures. SAM control of surface character has been used to direct the deposition of MOCVD metals, including Cu\textsuperscript{27,28}, Pd\textsuperscript{29} and Pt\textsuperscript{29}. The same mechanism was utilized to demonstrate device patterning of working multimaterial FERAM cells\textsuperscript{18}.

For this device, a two layer mask/stamp set was developed, with one monolayer pattern defining the deposition of both the bottom Pt electrode and the PZT cell, and a second monolayer pattern defining the top Pt electrode. The process flow for monolayer patterning and material deposition is shown in Figure 10. Following microcontact printing of an initial monolayer of OTS on a TiN//Si(100) wafer, an 800Å Pt film was selectively deposited by MOCVD from a bis(hexafluoroacetylacetonato)platinum [Pt(hfa)\textsubscript{2}] precursor at 350°C and 0.5 torr\textsuperscript{18}. As the monolayers are robust up to 400°C, the same monolayer resist was subsequently used to define the deposition of a PZT film, deposited by spin-coating a 0.3M methoxyethanol-based PbZr\textsubscript{0.53}Ti\textsubscript{0.47}O\textsubscript{3} sol-gel precursor. Following pyrolysis of the PZT film to 175°C, the PZT deposited above monolayer functionalized regions de-adhered and cracked, as observed for Ta\textsubscript{2}O\textsubscript{5} layers in figure 7. These poorly adhered, cracked regions were removed by polishing the entire wafer with cotton felt wet by isopropanol, leaving patterned PZT//Pt structures on the Si substrate. At this point, the second stamp pattern was used to microcontact print OTS monolayers atop the PZT, and selective deposition of Pt was again conducted to define the composite Pt//PZT//Pt//Si\textsubscript{3}N\textsubscript{4}/Si(100) structure.
At this point, the entire structure was fired to 700°C to crystallize the PZT and produce a working device structure. A profilometry cross section and the ferroelectric hysteresis of the composite devices are shown in Figure 11. It appears this same methodology could be applied to a broad variety of metal and ceramic systems for device patterning without need for lithography, wet chemical etching, or reactive ion etching of films.

V. Summary

Use of microcontact printing to define patterns of self-assembled monolayers appears to be a promising new method for patterning diverse materials including electroceramics, conductors, and magnetic materials. To date, this method has proven effective in patterning films deposited by several techniques, including sol-gel, MOCVD, and chemical precipitation. It is expected other techniques, including electrodeposition and hydrothermal processing, might also find utility for this method. The robust nature of self-assembled monolayers typically maintain a substrate’s patterned surface character to 400°C, allowing a variety of deposition processing conditions. Alternatively, the SAMs may be intentionally removed either by heating above this temperature, or by treatment in UV/ozone to decompose the SAM. Microcontact printing appears to be a straightforward, ambient processing method applicable to patterning a variety of materials. As the patterning is a non-serial, physical stamping method, the potential exists for high throughput and there is no fundamental optical size limit. In particular, patterned features in the 35-40nm range have been developed using this technique. The capability to pattern such fine feature sizes may accordingly allow deeper integration of electroceramics and other smart materials into future generations of microelectronics.
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References


Figure captions

Figure 1. Illustration of thiol and organosilane monolayers, and self assembly on a substrate.

Figure 2. Schematic outline of monolayer microcontact printing (μCP)\textsuperscript{7}.

Figure 3. Schematic of μCP monolayer patterning of sol-gel oxide thin films.

Figure 4. Topography-mode AFM image of 3μm wide, 25Å height OTS monolayer on silicon. The monolayer strip was microcontact printed\textsuperscript{2,3}.

Figure 5. Optical micrographs (a-c) and Auger electron spectroscopy (d) of selective LiNbO\textsubscript{3} deposition by monolayer patterning.

Figure 6. Heteroepitaxial, monolayer-patterned stripe waveguides of LiNbO\textsubscript{3} on sapphire, and selected area diffraction of LiNbO\textsubscript{3} on Al\textsubscript{2}O\textsubscript{3}.

Figure 7. Tantalum oxide film (a) before and (b) after oxide liftoff\textsuperscript{4,8}.

Figure 8. Complex shape, fine resolution, end edge structure of monolayer patterned Ta\textsubscript{2}O\textsubscript{5} films on Al//Si\textsuperscript{18}.

Figure 9. Stress evolution of oxide films for Ta\textsubscript{2}O\textsubscript{5}//Si and Ta\textsubscript{2}O\textsubscript{5}//monolayer//Si\textsuperscript{18}.

Figure 10. Schematic of two-stage microcontact printing patterning of Pt//PZT//Pt//TiN//Si ferroelectric memory cells\textsuperscript{18}.

Figure 11. Profilometry, illustration, and ferroelectric hysteresis of monolayer patterned FERAM cells\textsuperscript{18}. Hysteresis is compared to standard PZT 53/47 processed on sputtered Pt top and bottom electrodes.
Figure 1.

Alkanethiol monolayer

Organosilane monolayer

$X = \text{hydrophobic (CH}_3, \text{CF}_3, \text{ etc.) or hydrophilic (OH, COOH, etc.) tail group}$

Octadecyltrichlorosilane (OTS)

$X = \text{CH}_3 \text{ (hydrophobic)}$

6-30Å monolayer

Substrate
Figure 2.

PDMS

Substrate

“inked” with solution of OTS in hexane

SAMs of OTS (2-3 nm)


25Å monolayer
Figure 3.

1. Microcontact printing of OTS
   
2. Spin casting of sol-gel precursors and soft bake
   
3. Polishing and crystallization

PDMS “inked” with solution of OTS in hexane

Substrate

SAMs of OTS (2-3 nm)

Cracked film

Amorphous Oxide (>80 nm)

Crystalline Oxide (80 nm)
Figure 4.

Atomic force microscopy image of OTS printed 4μm monolayer strip
Figure 6

(c) TEM selected area diffraction

\(\text{Al}_2\text{O}_3\)  \(\text{LiNbO}_3\)  \(\text{LiNbO}_3/\text{Al}_2\text{O}_3\)
Figure 8

(a) Complex shape patterned \( \text{Ta}_2\text{O}_5 \) thin film on Si
(b) 4\( \mu \)m oxide features on Al/Si
(c) 100nm thick \( \text{Ta}_2\text{O}_5 \) on Al/Si
Figure 9
Capacitor Fabrication Steps

1. μCP OTS-First Level
   - Substrate
   - OTS

2. Pt-Bottom Electrode
   - Selective CVD at 350°C
   - Substrate
   - Pt

3. PZT-Ferroelectric
   - Spin cast by Sol-Gel
   - (soft bake at 175°C)
   - Substrate
   - Pt
   - PZT

4. Polish
   - Substrate
   - PZT
   - Pt
5 **µCP OTS-Second Level**

- OTS
- PZT
- Pt

Substrate

6 **Pt-Top Electrode**

Selecting CVD at 350°C

- Pt
- PZT
- Pt

Substrate

7 **Crystallization at 700°C**

- Pt(800Å)
- PZT(1000Å)
- Pt(1000Å)

Substrate

- PDMS

200 μm