Patterned Microstructure of Sol–Gel Derived Complex Oxides Using Soft Lithography**

By *Seana Seraji*, *Yun Wu*, *Nels E. Jewell-Larson*,
Michael J. Forbess, *Steven J. Limmer*, *Tammy P. Chou*, and
*Guozhong Cao**

While the semiconductor industry continues to push the limits of small-scale devices, the cost of the equipment needed to achieve such small geometries has also kept similar pace.[1] The average research lab does not have the funds to acquire, nor maintain the photolithographic and etching equipment needed to create such patterned structures. This unavailability of resources effectively prevents many groups from being able to perform research in cutting edge fields, such as microelectromechanical system (MEMS) technology, which require the ability to pattern a wide range of materials on a very small scale. Recently however, much attention has been given to a collection of non-photolithographic patterning techniques collectively known as soft lithography, which have the potential of becoming versatile and low cost methods for creating micrometer and sub-micrometer sized structures.[1–8] To date, several devices have been fabricated using soft lithographic techniques, such as polymeric field effect transistors (FETs),[2] electro-optic devices,[3,4] Schottky diodes,[5] and silicon metal oxide FETs (MOSFETs),[6] to name a few.

In addition to cost benefits, soft lithography has many advantages over traditional photolithography. Photolithography is very sensitive to surface topography. If the substrate to be patterned is not extremely flat, then acceptable results can not be obtained.[1] In contrast, since an elastomeric mold is used in soft lithography, good conformity over curved surfaces is possible, and thus non-planar substrates can be patterned with ease.[1] Material selection is another limitation of photolithography. Only photosensitive materials (such as photo-resists) can be directly patterned, and any other material that needs to be patterned must be susceptible to some type of etching technique.[2] These restrictions seriously limit the arsenal of materials that can be used. On the other hand, with soft lithography, any material that can be derived from liquid precursor can be patterned, provided that the solvent used does not swell the elastomeric mold.[2] Another benefit of this method is that it is an inherently mild process.[8] As a result, many chemically and physically sensitive materials such as dyes and biomolecules can be patterned using this technique, showing again the versatility of this process.[8]

As a result of the vast potential of these techniques, many reports describing the use of soft lithography to create pat-

terned structures can be found in the open literature.[1–8] However, most of these experiments were focused on relatively simple, single component oxide systems or polymeric materials.[1–8] No work on the direct patterning of complex oxide materials has been reported in the literature. However, these materials possess many important physical properties such as ferroelectricity, piezoelectricty, pyroelectricity, and high T_c superconductivity, which make complex oxides very useful for industrial and modern technological applications. For example, piezoelectric materials play a critical role in MEMS.[9] As such, it would be very beneficial to develop a convenient and low cost method of patterning these materials. This report describes our preliminary work on patterning complex oxide ceramics using soft lithography in conjunction with sol–gel processing. Pb(ZrTi)O$_3$ (PZT) and strontium niobate (Sr$_2$Nb$_2$O$_7$), both of which are piezoelectric ceramics, were chosen as model systems to form patterned structures on silicon substrates using soft lithography. Specifically, the microstructures were patterned by micro-molding in capillaries, or MIMIC molding.[1,2]

In the preparation of the Sr$_2$Nb$_2$O$_7$ sol, the inorganic precursors used were strontium nitrate Sr(NO$_3$)$_2$ (99 %) and niobium pentachloride (NbCl$_5$) (99.8 %). The procedure implemented is outlined in the flowchart, Figure 1, which differs from other reported methods.[10,11] Using ethylene glycol as a cross-linking agent and ethanol as a solvent, a transparent, stable sol was obtained. Although only 0.018 mol of water was added, hydrated citric acid was used, which provided the extra water needed to achieve the desired molar ratio of Sr/
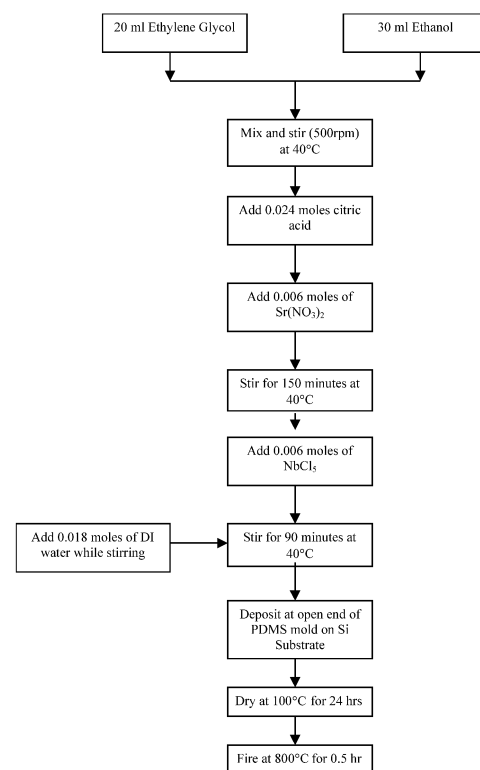

Fig. 1. Flowchart for Sr$_2$Nb$_2$O$_7$ patterning.

$Nb/H_2O = 1:1:3.5$. The final concentration of $Sr_2Nb_2O_7$ in the sol is of 0.6 M. This sol was used for creating the patterned structures with the soft lithography molds.

In contrast, the PZT sol was prepared using the following organometallic precursors (also commonly referred to as metal alkoxide precursors): $Pb(CH_3COO)_2$, $Zr(C_3H_7O)_4$, and $Ti((CH_3)_2CHO)_4$. The lead precursor was combined with acetic acid, while separately the zirconium and titanium precursors were mixed together. These two mixtures were then combined. Ethylene glycol and water were then added to this mixture. During the sol preparation, the alkoxide precursors were hydrolyzed (reacted) with H_2O to form hydroxides. Through condensation reactions, nano-sized clusters were formed.[12]

Figure 2 shows the X-ray diffraction (XRD) spectra of the PZT and $Sr_2Nb_2O_7$ xerogel samples derived from their respec-
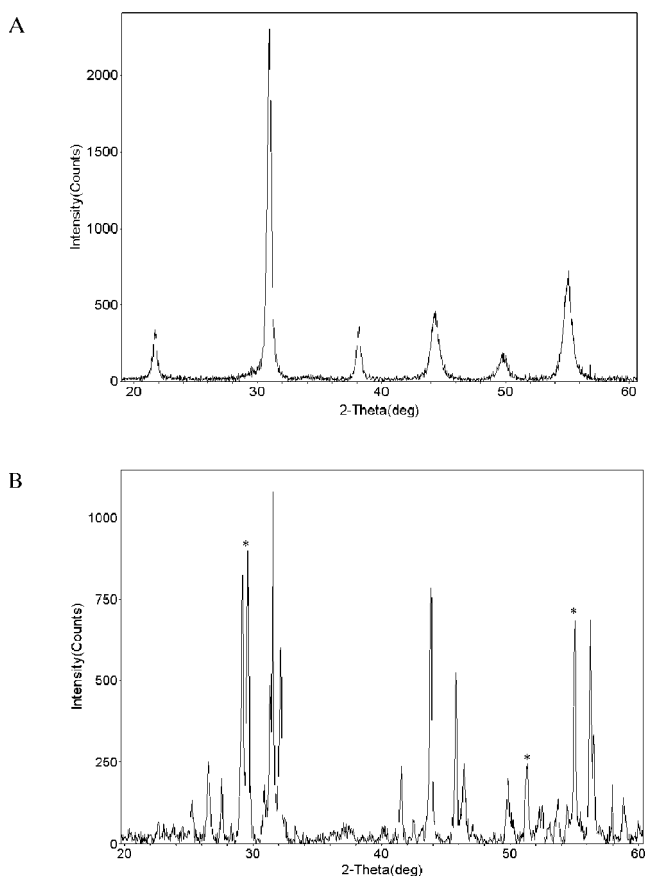

Fig. 2. XRD spectra for A) PZT, B) $Sr_2Nb_2O_7$. Both samples from sol–gel derived powders. (* Represents unidentified phases.)

tive sols. Xerogels were made from the sols, and then fired at 700–1000 °C for 30 min in air. The resulting powders were then ground and used for XRD analysis. A single phase PZT was formed, with no detectable second phases. In the $Sr_2Nb_2O_7$ system, $Sr_2Nb_2O_7$ was the major phase; however, a minor unidentified secondary phase was detected. XRD signals from patterned and crystallized arrays on (100) silicon wafers were rather weak, probably due to the small area and low coverage of patterned arrays. However, XRD spectra on

dip-coated films on silicon substrates were found the same as that shown in Figure 2, when the films and powders were subjected to the identical heat-treatment.

The process of soft lithography has been thoroughly described in many other publications, therefore only a brief description will be given here.[1,2] A positive master is first created on a silicon wafer using standard semiconductor processing techniques. The master is then covered with liquid polydimethylsiloxane (PDMS). When the PDMS has cured, the silicon and PDMS are separated, and thus a negative of the pattern is transferred to the PDMS. For this study, a two by two micrometer channel PDMS mold was made using this procedure.

The molds were then thoroughly cleaned with ethanol. The molds were then placed in conformal contact with a clean silicon substrate. The channels of the mold thus formed capillaries with the silicon substrate. The sol was then deposited at the open end of these capillaries with a transfer pipette. Through capillary force, the sol was drawn into the mold.[1]

The molds and substrates were then placed in a drying oven for 24 h at 100 °C, to drive off the solvent. As the solvent evaporated, the condensation reaction proceeded, thus promoting cross-linking between individual clusters, leading to the sol–gel transition. After the materials had gone through their sol–gel transitions, the molds were carefully removed, leaving behind positive replicas of the molds on the surface of the silicon. (PDMS has a relatively low surface energy, and therefore the material preferentially remains on the silicon substrate.[2]) The patterned structures were then fired at 700 and 800 °C for 30 min for the PZT and $Sr_2Nb_2O_7$ patterned structures respectively in order to densify the structures and to form the desired phases. The topography and morphology of these structures were then analyzed by both atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Figure 3, parts A and B, are AFM micrographs of the 2 μm × 2 μm PZT patterned structures, before and after firing, respectively. Since the concentration of the sol used was rather low, a significant amount of shrinkage was expected. The pre-firing height of the arrays was (on average) approximately 0.35 μm, which was significantly smaller than the 2 μm mold. This was not surprising, for it is well known that solvent evaporation in a wet gel is accompanied by significant shrinkage.[13] The relatively low pre-firing height may also be a result of insufficient mold filling. It is possible that the capillary force in the channel was not great enough to cause the sol to completely fill the mold.

During sintering, further shrinkage was observed. Approximately 46 % linear shrinkage was observed in the vertical direction. Despite the significant shrinkage, macroscopically uniform, crack free patterned structures were obtained, as can be seen from the SEM picture (Fig. 3C). Continuous grooves running along the tops of the channels were also observed after firing. The cause of this is debatable; however it is believed that the groove formation is a result of a density gradient, and the slip-casting effect. When the sol fills the molds, the solvent will in part permeate through the mold to evaporate, causing a build up of solid material along the walls of the
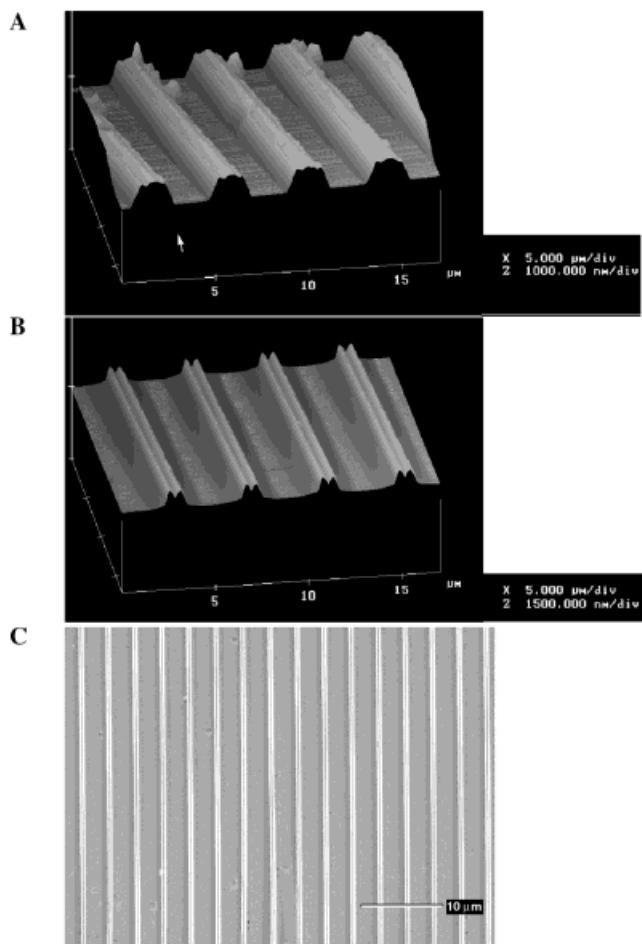
A

B

C

Fig. 3. A) PZT sample before firing (AFM). B) PZT sample after firing (AFM). C) PZT sample after firing (SEM).

A

B

C

Fig. 4. A) $Sr_2Nb_2O_7$ sample before firing (AFM). B) $Sr_2Nb_2O_7$ sample after firing (AFM). $Sr_2Nb_2O_7$ sample after firing (SEM).

mold.[14] This can result in a structure that has a shell more dense than the inner material. As the material was fired, the top of the structure collapsed, due to the greater extent of shrinkage that occurred in the more porous inner gel, thus causing the observed groove to develop along the top.

Figures 4A and B are AFM micrographs of unfired and fired 2 μm × 2 μm $Sr_2Nb_2O_7$ channels, respectively. The initial height of this pattern (0.673 μm) was also found to be significantly smaller than the 2 μm mold. The $Sr_2Nb_2O_7$ sol was much more viscous than the PZT, and thus might not have dried completely after 24 h at 100 °C. As a result, the unfired samples appear to be somewhat larger than the PZT samples. When fired though, this sample exhibited shrinkage of approximately 85 % in the vertical direction whereas the horizontal shrinkage of this sample was negligible. This shrinkage behavior is significantly different from that of the PZT sample. This phenomenon might imply that no dense shell was formed during drying. Figure 4C is a SEM micrograph of the strontium niobate sample and indicates that no macroscopic cracks were formed. SEM micrographs with higher magnification (not shown here) also reveal no detectable microscale cracks.

Another observation made involved the fidelity of the mold replication. The molds used for this study were all rectangular
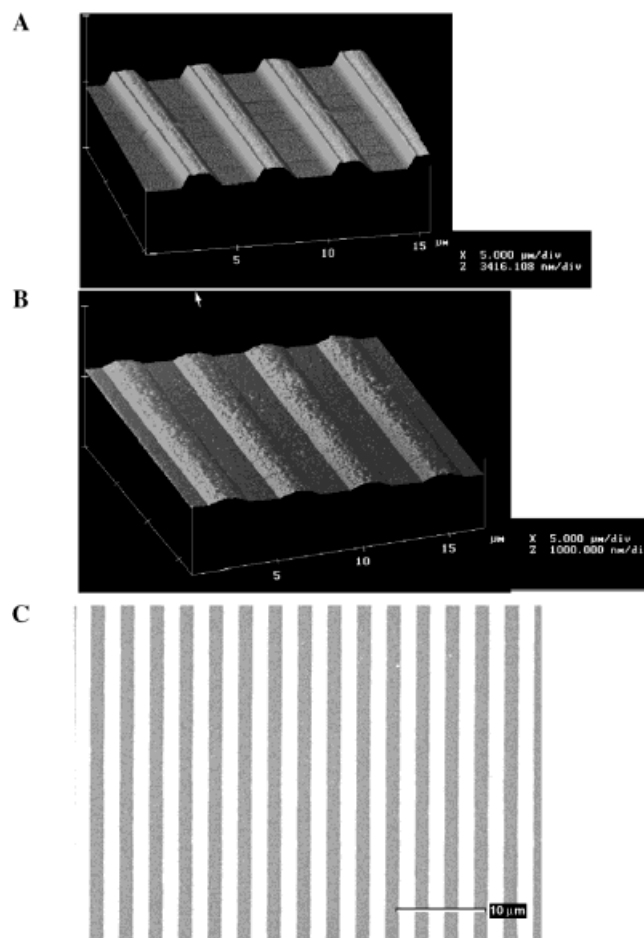
with sharp 90° side walls. However, as can be seen from Figures 3 and 4, the side walls of the resulting patterns were tilted to varying degrees. This effect was even more pronounced after firing. One possible explanation is that the bottom edge of the channel was constrained by its adhesion to the silicon substrate, while the top of the channel was free of constraints. Thus, the top was free to shrink in any direction, while the bottom could not contract in the horizontal direction, which would give rise to a slanting of the walls of the channels.

In summary, a procedure for patterning complex, multi-component piezoelectric ceramics (with PZT and $Sr_2Nb_2O_7$ as a model system) using micro-capillary molding in conjunction with sol-gel techniques was described. Macroscopically crack free and uniform microstructures were obtained and the desired crystalline phases were formed after firing at high temperatures. However, significant shrinkage was found in the patterned structures prior to and after firing. Such shrinkage resulted in not only a dimension change, but also a distortion of the shape of the structure. A higher load of solid constituents should reduce the shrinkage. In addition the formation of a dense outer shell seems to be effective in minimizing shape distortion.

[1] Y. Xia, G. M. Whiteside, *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.
[2] W. S. Beh, I. T. Kim, D. Qin, Y. Xia, G. M. Whitesides, *Adv. Mater.* **1999**, *11*, 1038.
[3] J. T. Rantala, G. E. Jabbour, J. Vahakanagas, S. Honkanen, B. Kippelen, N. Peyghambarian, *Jpn. J. Appl. Phys., Part 2 (Lett.)* **1998**, *37*, L1098.
[4] J. A. Rogers, M. Meier, *56th Annu. Device Res. Conf. Dig. IEEE*, New York **1998**, p. 134.
[5] J. Hu, R. G. Beck, R. M. Westervelt, G. M. Whitesides, *Adv. Mater.* **1998**, *10*, 574.
[6] N. L. Jeon, J. Hu, G. M. Whitesides, M. K. Erhardt, R. G. Nuzzo, *Adv. Mater.* **1998**, *10*, 1466.
[7] M. J. Lochhead, P. Yager, *Int. Soc. Opt. Eng.* **1997**, *3136*, 261.
[8] Y. Xia, G. M. Whiteside, *Adv. Mater.* **1996**, *8*, 245.
[9] D. L. Polla, L. F. Francis, *MRS Bull.* **1996**, *July*, 59.
[10] A. V. Prasadaro, U. Selvaraj, S. Komarneni, *J. Mater. Res.* **1995**, *10*, 704.
[11] K. Okuwada, S. Nakamura, H. Nozawa, *J. Mater. Res.* **1999**, *14*, 855.
[12] G. Yi, M. Sayer, *Ceram. Bull.* **1991**, *70*, 1173.
[13] C. J. Brinker, G. W. Scherer, *Sol–Gel Sciences*, Academic, San Diego, CA **1990**.
[14] J. S. Reed, *Principles of Ceramic Processing*, Wiley, New York **1994**.

Novel Chromogenic Polymer Gel Networks for Hybrid Transparency and Color Control with Temperature

By *Arno Seeboth*,* *Jörg Kriwanek*, and *Renate Vetter*

In the last decade chromogenic materials that respond to stimuli such as changes in temperature or electric fields with reversible changes in their transparency have been developed.[1,2] Among these chromogenic materials, the thermotropic materials reversibly turn at a definite temperature or in a variable temperature range from a transparent into a milky white and reflective state. In the milky white state they act as light[3] or heat filters.[4] One of the most important motivations for all efforts in developing such switchable materials is their potential technical application in the external glazing of buildings for sun protection.[1,2,5]

Recently we reported on the first example of reversible thermochromism of phenol-substituted dyes embedded in transparent hydrogels, due to temperature-induced shifts of the proton-transfer equilibrium between the phenol and phenolate form of the dye molecules in the polyvinyl alcohol/borax/surfactant gel network.[6]

In this paper a gel for hybrid transparency and color control with temperature is presented for the first time. The novel chromogenic material, prepared by mixing a polyalkoxy derivative and an aqueous LiCl solution with a suitable dye, combines the advantages of a thermotropic and a thermochromic material in one. Furthermore the working temperature range for the dye-containing gel network is extended down to –20 °C.

Gels composed of polyalkoxy-derivatives/salt/water with a water content of 25 % can reversibly change their temperature–transparency behavior.[2,7] The changes in transparency of these thermotropic gels are due to the formation of lyotro-

pic liquid-crystalline (LC) phases as well as phase separation. We looked for appropriate dyes that would exhibit thermochromism in such gel networks without destroying the thermotropic properties on the one side and the gel behavior on the other side. However it is well known that adding small amounts of additional components to a LC system or to a gel will lead to specific changes of the macroscopic properties. By testing a series of indicator dyes embedded in a polyalkoxy/LiCl/water gel network, which itself (i.e., without dye) becomes white and reflective in the temperature range of 36–40 °C, the phenol-substituted indicator dyes Chlorophenol Red, Nitrazine Yellow, and Bromothymol Blue were found to exhibit thermochromism. In the presence of Nitrazine Yellow the color changes gradually from blue at ≤ 25 °C to green above 33 °C, while for Chlorophenol Red a color change from red at ≤ 5 °C to yellow above 32 °C was observed. On the thermochromic behavior of the Bromothymol Blue (BB, Fig. 1) containing gel network we report in detail.
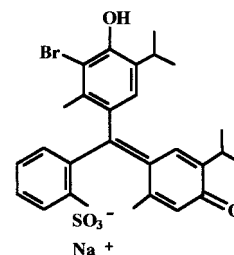

Fig. 1. Molecular structure of the dye Bromothymol Blue (BB).

For the polymer, a polyalkoxy derivative of molecular weight 4800 with a propylene oxide proportion of 87 % and an ethylene oxide proportion of 13 % was used. The gel was prepared by mixing the polyalkoxy derivative with LiCl, an aqueous buffer solution, and BB. After homogenization through leaving the gel mixture at room temperature for some hours, we obtain a transparent green gel. Raising the temperature, the gel becomes transparent yellow at a temperature of 33 °C. This thermochromic behavior is illustrated
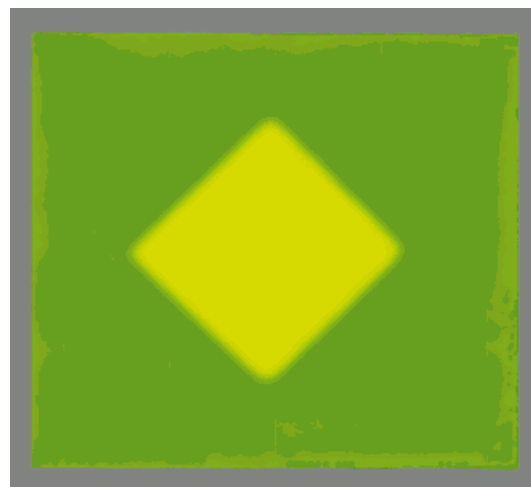

Fig. 2. Illustration of the thermochromic behavior of a BB-containing gel probe between two glass plates (2 mm thickness). By warming up a quadratic area from room temperature to 33–34 °C the transparent green state becomes transparent yellow.

[*] Dr. A. Seeboth, Dr. J. Kriwanek, R. Vetter
Department of Functional Materials
WITEGA, Applied Materials Research Co. Ltd.
D-12489 Berlin (Germany)
E-mail: a.seeboth@witega.de