Patterning of $BaTiO_3$ Nanostructures Using Modified Micromolding in Capillaries

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Abstract

There is a continuing need for patterning multifunctional materials to harness their features and explore synergy among diverse properties and phenomena. Soft lithography, among various patterning techniques, is a versatile method that can generate inorganic patterns in a parallel mode. Experimentation was performed making use of flexible soft lithography to fabricate miniature patterns of a complex multifunctional oxide, $BaTiO_3$. Specifically, a modified method of micromolding in capillaries (MIMIC) was used with sol-based starting materials. Modifications of MIMIC consisted of an O_2 plasma treatment to the surface of the mold and substrate and the use of a thin-film mold. Nanoscale features (~50nm) were produced with this modified method and examined using atomic force microscopy (AFM) and scanning electron microscopy (SEM). The patterns were found to be highly dense, uniform, and continuous over a relatively large area. These modifications to the traditional MIMIC technique were significant; the resulting method proved to be simple and effective in producing the desired patterns.

Introduction

Multifunctional oxides have been under extensive research for use in miniaturized patterning due to their special properties that offer a wide range of applications in the development of new electric, magnetic, and optical devices. Patterning is the avenue for increasing capabilities to explore the phenomena of materials and structures at levels that are becoming increasingly smaller. Currently, attention is focused on fabrication at least one feature less than 100 nm in length.

There are many techniques employed for patterning miniature structures. Conventional patterning techniques are commercially available and have brought great technological advances in microelectronics and other fields. One of the most prominent examples is photolithography. Photolithography is a widely used patterning technique that utilizes photocurable polymers to define miniature patterns and transfer them to metal or semiconductor substrates using wet or dry chemical etching. However, even such a commonly used technique as photolithography has its drawbacks. For many functional ceramics, photolithography can be limited by the inherent chemical stability of the materials. For instance, dry etching with lead zirconium titanate ($PbZr_xTi_{1-x}O_3$, PZT) will usually be very slow and costly due to the requirement of specialized equipment to avoid deleterious lead contamination.[1] Wet chemical etching also can cause shape irregularity in final structures.[2] With many other techniques in use, extensive research has been employed in the development of unconventional lithography techniques, like soft lithography, to serve as alternatives and meet the shortcomings of conventional techniques. This is especially important when patterning nonstandard features (e.g., nonplanar substrates or three-dimensional fabrication) and relatively fragile materials, such as organic materials.[3]

Soft lithography refers to patterning techniques that use a soft mold to transfer patterns to a surface in which liquid precursors are used as starting materials.[3] These are simple, low-cost techniques with high output and are compatible with the patterning of sensitive organic materials. Some common forms of soft lithography in further development are microcontact printing (μCP), dip-pen nanolithography (DPN), and micromolding in capillaries.

The focus of this research is the modification of a specific patterning method, MIMIC, and its application to the patterning of multifunctional oxides (e.g., $BaTiO_3$). MIMIC has proven reliable and easy to perform. Some advantages are found in its unconventional fabrication capabilities, including three-dimensional shapes, structures on nonplanar surfaces, and complex patterns beyond those of simple, criss-crossed lines.[4] In the past, MIMIC has been used to fabricate structures with microscale features.[5] However, there are challenges when attempting to use traditional MIMIC to fabricate structures with nanoscale features. This research presents a modified form of MIMIC. The intent is to prove the effectiveness of these modifications in pushing the use of MIMIC to fabrication at the nanoscale and to demonstrate how this modified method can make use of $BaTiO_3$ in producing such nanostructures.

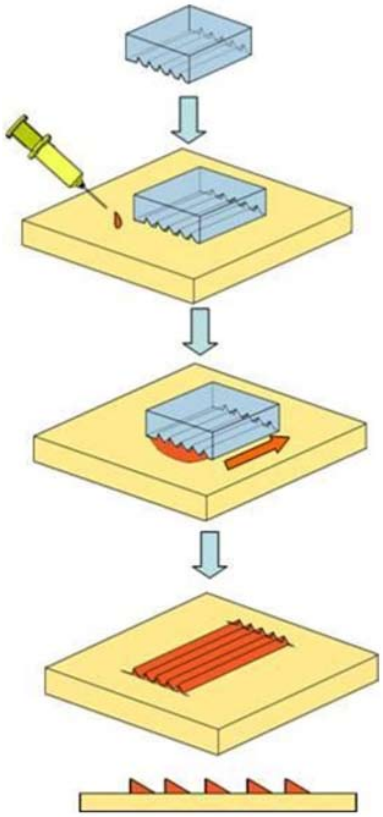

Figure 1: Diagram of the traditional MIMIC procedure. A mold with an imprinted pattern is placed on a substrate. Filling liquid is applied along an edge with open channels. The mold and substrate are dried together; the mold is then removed to reveal the underlying structures.

Background

The modified MIMIC technique examined in this study was tried using $BaTiO_3$. $BaTiO_3$ is of particular interest due to its desirable ferroelectric and piezoelectric properties. Current research with ferroelectric ceramics is important in the development of specialized devices such as capacitors, high-density memory, and new mechanisms ready for Boolean coding. $BaTiO_3$'s piezoelectric properties offer a range of applications in the improvement of microelectronic capabilities, including voltage generation, frequency control, and other special utilities.

This experiment utilized the sol-gel approach for synthesizing $BaTiO_3$ as a starting material. Sol is defined as a suspension of colloidal particles. Concerning the preparation of oxide materials, these colloidal systems are produced by the condensation of hydrolyzed ions. In the case of $BaTiO_3$, these ions are metal alkoxides.[6] The use of sol-gel as a starting material has been widely accepted as a simplified and versatile approach due to its ease of use, low-temperature synthesis, low cost, and avoidance of extreme pH conditions.

Although there are advantages of traditional MIMIC over other general types of patterning, there are also shortcomings. The procedure used with traditional MIMIC can be described in the following way (Figure 1). First a soft mold, commonly made of polydimethyl-siloxane (PDMS), is applied to the surface of a substrate. This mold has a hydraulically continuous design imprinted on its face. It is placed on top of the substrate with the design in contact with the surface of the substrate. The extruding features of this design create channels when they are in contact with the surface of the substrate; a liquid-phase precursor is then applied at the opening of these channels. The liquid is drawn into the channels by natural capillary forces. This fixture of mold and substrate is then dried. Finally, the mold is detached, leaving the miniature structures of the applied precursor in a solid phase.

The dilemma with traditional MIMIC is in the transition from producing features on the microscale to producing features on the nanoscale. In this transition, the traditional method meets two serious problems: achieving a proper infiltration speed and maintaining conformal contact between mold and substrate.

The infiltration speed of the channels is directly related to the cross-sectional area of each channel.[4] To make smaller patterns, the cross-sectional area of each channel must be reduced, thereby compromising the infiltration speed of the channels. In addition, the filling liquid is constantly evaporating during the infiltration process. This evaporation increases the liquid's viscosity and thus slows infiltration speed. These retarding factors can have the cumulative effect of stopping the infiltration of a liquid before it meets its preferential length. This presents problems when attempting to pattern larger areas.

Maintaining conformal contact and, consequently, the preservation of the original shapes of protruding features when in contact with a surface is important for several reasons. The first reason is to prevent feature distortion. If proper contact is not achieved, channels may wedge-out or wedge-in when in contact with a surface, causing a distortion in the structures produced.

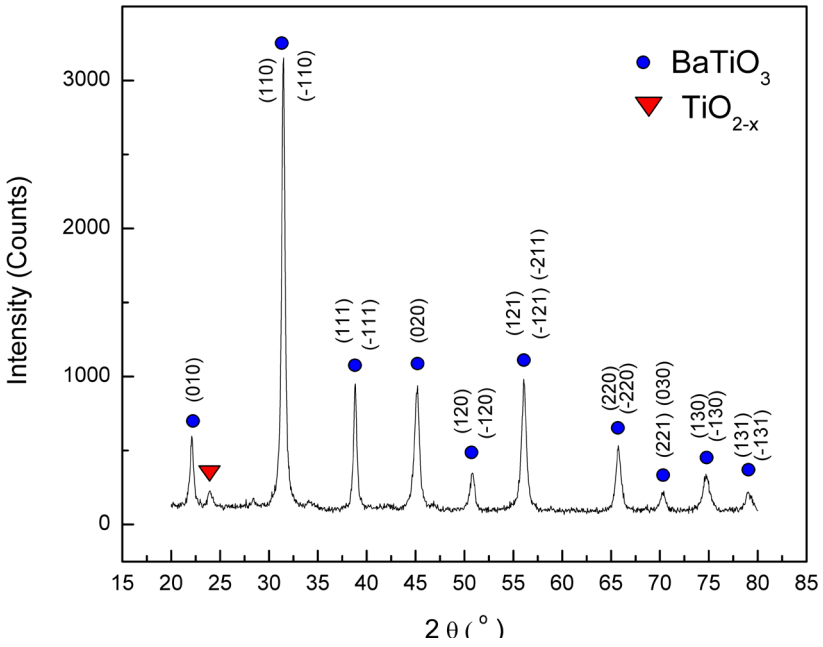

Figure 2: XRD pattern of $BaTiO_3$ powder annealed at 700 °C for 1 hr.

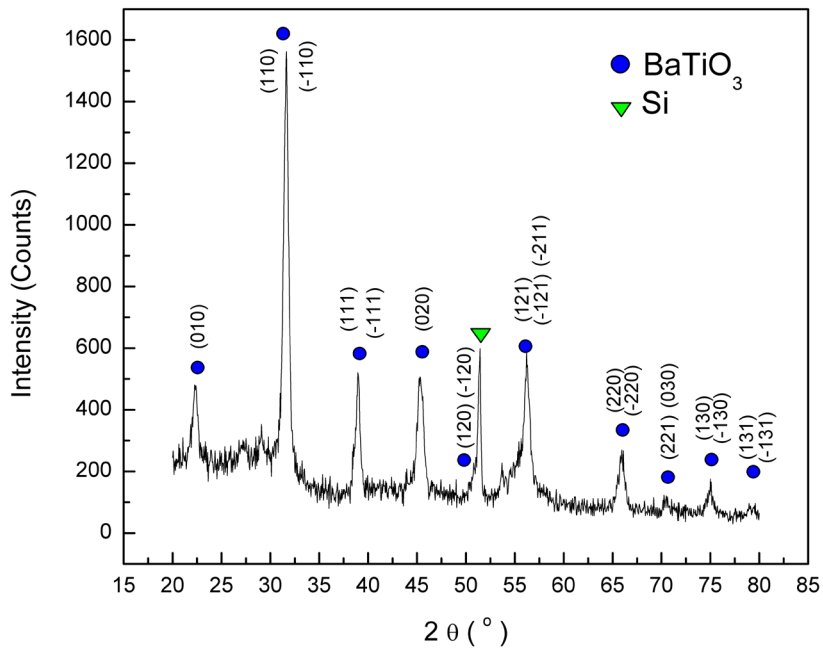

Figure 3: XRD pattern of $BaTiO_3$ thin film annealed at 750 °C for 1 hr. Sol was spin-coated on a silicon substrate at 4,000 rpm for 30 sec. The thickness of this thin film was very close to the thickness of the miniature $BaTiO_3$ structures produced.

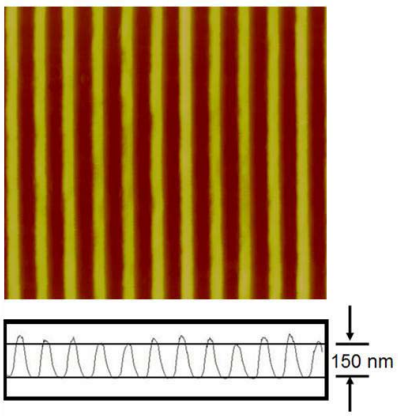

Figure 4: (Before annealing) AFM image with its corresponding cross-sectional file of $BaTiO_3$ miniature structures before being annealed. The average height of the features was ~ 150 nm; the average width was ~ 350 nm.

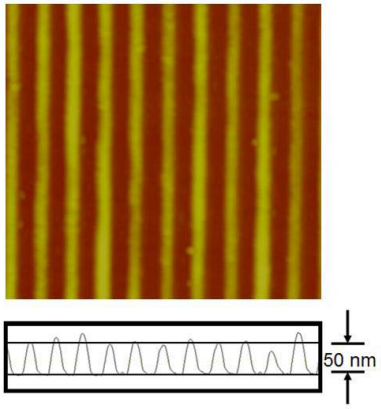

Figure 5: (After annealing) AFM image and corresponding cross-sectional file of the $BaTiO_3$ miniature structures after they were annealed. The average height of the features was ~ 50 nm; the average width was ~ 230 nm.

In order to obtain high-density features, the width between channels must be reduced. Reducing the width makes channels more liable for cross-talk, meaning the channels are more prone to bend and intersect each other if conformal contact cannot be maintained everywhere. Cross-talk changes the pattern in the mold and allows the filling liquid to flow in undesignated regions, producing chaos in patterns. Theoretically, conformal contact can be maintained by applying appropriate pressure to the top surface of the mold. However, determining the right pressure and how to correctly apply this pressure presents many challenges. This is especially relevant with high-density patterning of very small features. Modifications have been attempted in an effort to resolve these dilemmas. For example, vacuum pressure was used to obtain improved conformal contact and faster infiltration speed.[5] The results showed increased infiltration speed with regularly produced patterns. However, this modification requires the use of devices designed specifically for this procedure. It is highly favorable to develop a more general approach to circumvent these drawbacks and to produce features reduced to the nanoscale.

Described in the following procedure are simple modifications on traditional MIMIC that greatly improve conformal contact and infiltration speed.

Approach

The procedure was split into two phases: the synthesis of $BaTiO_3$ sol and the modified MIMIC procedure.

Sol Synthesis

This procedure was adapted from an article entitled "Optical and electrical properties of sol-gel derived $BaTiO_3$ films on ITO coated glass."[7] Titanium butoxide [$Ti(O\text{-}Bu)_4$] was first mixed with acetyl acetone (AcAc), maintaining a 1:8 molar ratio between $Ti(O\text{-}Bu)_4$ and AcAc. Next, $Ba(Ac)_2$ was dissolved in a 50:50 mixture of water and acetic acid. This $Ba(Ac)_2$ solution was then added dropwise to the $Ti(O\text{-}Bu)_4$/AcAc solution with rapid stirring to form a sol precursor with a 1:1 ratio of Ba to Ti.

X-ray diffraction (XRD) studies were performed on $BaTiO_3$ powders and thin films in order to prove the phase purity and study the phase transformation of the sol. The powders were made by evaporating $BaTiO_3$ sol at ~ 150° C for 24 hr and then annealing it at 700° C for 1 hr. The $BaTiO_3$ thin films were prepared by spin-coating the sol at 4,000 rpm for 30 seconds on Si (001) substrates that had been O_2 plasma cleaned prior to sol-spinning. Subsequently, the substrates were dried at 150° C for 30 sec and then pyrolyzed at 400° C for 2 min. This process of spinning and heating was repeated between one and five times on different substrates. Finally, the thin films were annealed at 750° C for 1 hr. XRD characterization was carried out using a Rigaku ATX-G x-ray diffractometer. For thin films, a Cu target was used with a working voltage of 50 kV, a current of 240 mA, and a glancing angle scan with the incident angle (Ω) set equal to 0.5°. For powders, $\theta/2\theta$ scans were made using a working voltage of 40 kV and a current of 20 mA.

Modified MIMIC Procedure

PDMS prepolymer was mixed with a curing agent (Sylgard® brand 184 silicone elastomer and curing agent) with a 10:1 volumetric ratio of PDMS to curing agent. After mixing, air bubbles were evacuated by placing the mixture in a vacuum chamber for ~ 30 minutes. The PDMS was then spread onto the surface of a gold grating (Edmond Optics® stock number NT43-852) with microscopic grooves patterned on one surface (1,200 groves per mm). These groves are "cut" at an angle, making a sawtooth pattern on the surface of the grating. The gaps between the "teeth" of this sawtooth edge serve as channels to be filled by a liquid precursor. The filling liquid takes the shape of these gaps and, when dried, becomes a series of very long wedges or ridged lines (Figure 1). The PDMS was spin-coated onto the surface of the gold grating at 4,000 rpm for 30 sec. This spin-coating process was performed three times in order to achieve the preferred thickness. The gold grating, coated with PDMS thin film, was then dried at ~ 70° C for 24 hr. After drying, the PDMS thin film was carefully peeled from the surface of the master mold.

The next step was to treat the imprinted surface of the thin-film mold and Si (001) substrates with O_2 plasma. O_2 plasma treatment was performed under 75W RF power, 50 sccm O_2 flow rate, and 75 torr backpressure for 20s. The thin-film mold and substrate were then cut into sizable pieces. A minor amount of isopropanol was applied to cover the surface of one of these substrate pieces and allowed to sit until it nearly evaporated. A piece of the thin-film mold was then placed on the substrate with the imprinted side down. The isopropanol was applied to facilitate an even spreading of the PDMS thin film. This fixture of thin film and substrate was left to sit until the isopropanol had evaporated completely.

With the mold in contact with the substrate, the channels were formed. $BaTiO_3$ sol was then applied at the opening of the channels. A small amount of liquid applied along one length of the mold may be sufficient to produce a successful infiltration of the channels, although multiple applications may be necessary.

Once the channels had been filled to their capacities, the mold and substrate were dried at ~ 70° C for two days. Now that the liquid in the channels had solidified, the mold was gently peeled off the substrate. Finally, substrates were annealed at 750° C for 1 hr. The modified MIMIC procedure was then complete.

The structures produced by the modified MIMIC process were examined using AFM (a Nanoscope III microscope [Digital Instruments, USA]) and SEM (a Quanta 600F SEM [FEI Company, USA]).

Results and Discussion

The XRD pattern shown in Figure 2 was made by a $BaTiO_3$ powder annealed at 700° C for 1 hr. The peaks show the $BaTiO_3$ crystallized after the annealing treatment. The peak positions correspond well with that of the desired tetragonal structure of $BaTiO_3$, although a minor impurity of titanium oxide is present. Figure 3 shows an XRD pattern of a $BaTiO_3$ thin film on a Si (001) substrate. Again, the peaks illustrate the proper crystallization and tetragonal structure of $BaTiO_3$. The thickness of

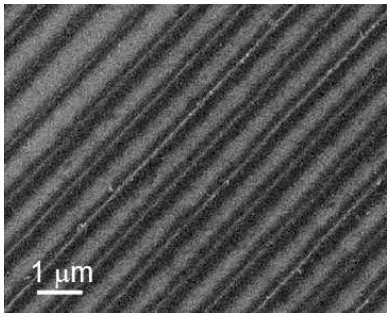

Figure 6: SE SEM image of the miniature $BaTiO_3$ structures.

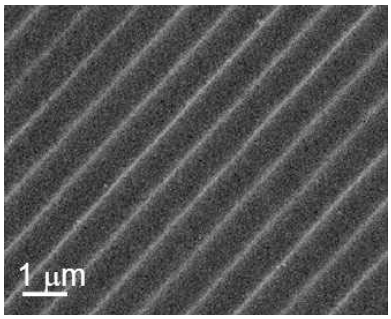

Figure 7: BSE SEM image of the miniature $BaTiO_3$ structures obtained from the same area as in Figure 6.

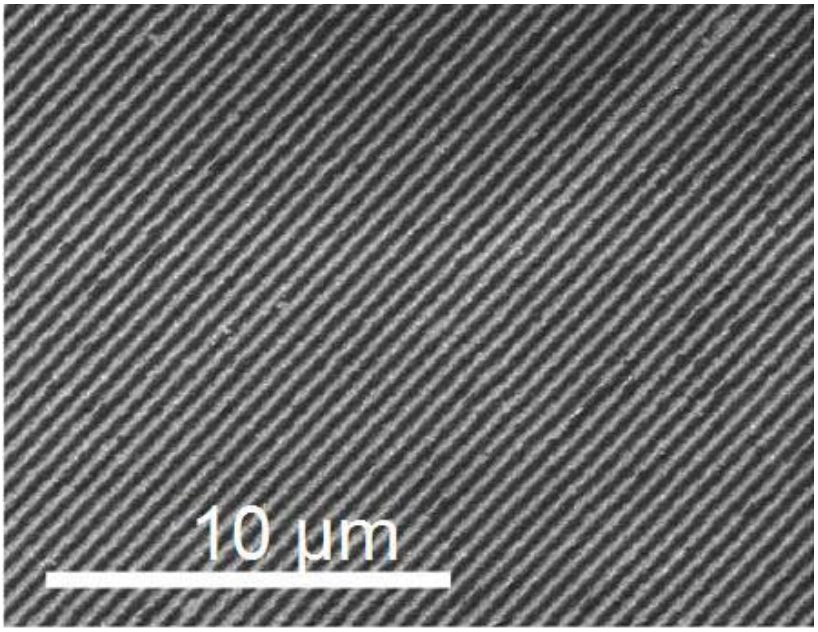

Figure 8: Large-area scan SE SEM image of the miniature $BaTiO_3$ structures.

the thin film is very close to the height of the structures produced using the modified MIMIC procedure; the two are within tens of nanometers of each other. Therefore, information derived from XRD studies on the thin film served as an appropriate reference to understand the phase composition of the actual structures produced with the modified MIMIC procedure.

AFM and SEM was used to study the topography and feature size of the miniature $BaTiO_3$ structures. Figure 4 shows an AFM image, along with its corresponding cross-sectional file, of the $BaTiO_3$ miniature structures produced before being annealed. The AFM image illustrates that the structures are continuous and of uniform shape; only minor deformations appear along the edges. The cross-sectional file illustrates that the cross-sectional pattern of the structure is periodic. The average height and width of these features before annealing were ~ 150 nm and ~ 350 nm. Figure 5 shows an AFM image and cross-sectional file of the same $BaTiO_3$ structures after they had been annealed. After annealing, the average height of the features was ~ 50 nm. The average width of the features was ~ 230 nm. The reduction of the height and width of the features after annealing results from both the elimination of organic components in the structures and the phase change from an open-structured, amorphous state to a dense, crystalline structure. These images and numbers illustrate the feasibility of this modified technique in preparing controlled nanoscale patterns. Using a nominal number of steps, this process was able to produce structures with features as small as 50 nm.

SEM images were complementary to the AFM images in mapping the size and shape of the structures. Figure 6 is a secondary electron (SE) SEM image of a small scan area of the $BaTiO_3$ structures. Figure 7 is a back-scattered electron (BSE) SEM image of the same area as in Figure 6. These images allow for a comparison between a topographic image (detailed by the SE image) and an image derived from the contrast of varying atomic weights of featured substances (detailed by the BSE image). In BSE images, areas having a larger average atomic number appear brighter. Barium and titanium are both heavier substances than silicon. Thus in Figure 7, the white lines represent concentrations of these heavier substances, indicating patterned structures of $BaTiO_3$. The black background represents the lighter silicon substrate on which these structures are resting. These details from both images confirm that the features viewed are in the shape of ridged lines and composed of $BaTiO_3$. Figure 8 is an SE image of a larger area scan of the $BaTiO_3$ structures; it provides further confirmation of these details showing the patterns to be consistent over a larger area.

These AFM and SEM results demonstrate that the modified MIMIC procedure successfully fabricated nanoscale, high-density ceramic patterns over a large area. The critical differences between this modified procedure and traditional MIMIC are the employment of a thin-film PDMS mold and an O_2 plasma treatment on the mold and substrate. In contrast to what can be done

with a bulk mold, using a thin-film mold allows for easy and even spreading without compromising patterning fidelity. The O_2 plasma treatment changes the surface energy of the mold and substrate and, consequently, reduces the contact angle between these two surfaces and the filling liquid.[4] Since the filling rate of the liquid is directly proportional to the cosine of this contact angle,[4] reducing this angle increases the filling rate. In addition to this, the plasma treatment induces a stronger adhesion between the surfaces of the mold and substrate. The cumulative effect of these modifications dramatically increases sol infiltration speed. For example, without the O_2 plasma treatment, complete infiltration could take 2 hr, given a small group of channels with lengths around 1 cm; after treating the mold and substrate, infiltration in the same experiment would near completion in about 30 sec. Collectively, these modifications have increased filtration speed while simultaneously reducing complications made by cross-talk and feature expansion.

The smallest feature dimension produced with this method was ~ 50 nm. One may ask, "How small can these MIMIC features be reduced?" Two very important issues must be addressed to answer this question. The first concerns the limitations of current lithography techniques; the size of the features on the master mold used in the MIMIC procedure is directly limited by the lithography technology used to make it. The second issue is determining what will be the final size of these MIMIC-produced features. How small will remaining features be after the process of infiltration, drying, and annealing? The volume of the filling material is reduced at each one of these steps. Knowing beforehand the consequence of these reductions is no trivial guess. A proper estimation of the limit for feature reduction using the MIMIC method remains very complicated.

Conclusions

A modified MIMIC technique was used to produce nanopatterns of $BaTiO_3$ from its sol precursor. With the use of a thin-film mold and an O_2 plasma treatment, problems concerning cross-talk and feature distortion were greatly reduced. The modifications increased infiltration speed and provided the capability to pattern sol-gel based materials at the nanoscale level using MIMIC. A sol-gel method was employed to make the $BaTiO_3$. XRD studies of $BaTiO_3$ thin films and powders showed the crystallization of $BaTiO_3$ to be in accordance with the desired tetragonal structure. The $BaTiO_3$ structures produced were in the form of ridged parallel lines. The lines produced were ~ 150 nm in height and ~ 350 nm in width before being annealed; they were reduced to ~ 50 nm in height and ~ 230 nm in width after being annealed. AFM and SEM images showed the patterns to be continuous and uniform in shape. This modified method of MIMIC proved simple in use and effective in producing the desired nanostructures.

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