LETTER

Stacks of Functional Oxide Thin Films Patterned by Micromolding

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ABSTRACT Stacks of up to five relief patterned functional oxide thin films were obtained by a low-cost and low-tech soft-lithographic patterning technique. Micromolding was used to pattern a film of a metal-organic precursor solution for Y-stabilized ZrO_2 (YSZO). Subsequent drying and pyrolysis yielded a line-patterned YSZO film. The process was repeated up to four times with a precursor solution for $BaTiO_3$ on top of the YSZO film, resulting in stacks of YSZO and $BaTiO_3$ lines with well-defined edges. This approach presents a step forward on the way to a versatile additive micropatterning technique with which simple multi-material device structures can be fabricated in a reliable, fast, and cost-effective manner.

KEYWORDS: micromolding • soft-lithography • oxides • micropatterning • sol−gel

INTRODUCTION

Fast, cheap, and reliable methods to replicate functional metal oxide-based micropatterns on relatively large areas of arbitrary substrates will enable the economically feasible construction of a wide variety of new devices. Examples of applications that would employ micropatterned oxides are data storage devices; infrared, gas, or magnetic field sensors; optical arrays; photocatalytic devices; and solar cells. Oxide micropatterns can be realized by the well-known soft-lithographic techniques (1), a family of replicative printing and molding techniques that employ an elastomeric mold or stamp with a relief pattern on its surface. One of the steps in all soft-lithographic processes involves conformal contact of the elastomer with a substrate, and using the elastomer as stamp or mold. Examples of micropatterned oxide films derived by soft-lithographic methods include (Pb,Zr)TiO_3 (2−4), ZrO_2 (5, 6), SnO_2 (5), (Ba,Sr)TiO_3 (7), and $SrBi_2Ta_2O_9$ (8). We used micromolding in combination with chemical solution deposition to micropattern ZnO (9), yttrium-stabilized zirconia (ZrO_2:8 % Y_2O_3, YSZO), $CoFe_2O_4$, $BaTiO_3$, and $BiFeO_3$ thin films, and have been able to generate arbitrary features of Pb(Zr,Ti)O_3 on silicon with lateral resolutions down to 100 nm (10).

In the present communication, we demonstrate the possibility to extend the micromolding technique to successively line-pattern several layers of oxides with micrometer-range lateral resolutions on Si (001) substrates, without the need for any intermediate etching and/or planarization steps (11). For the construction of most device architectures with micrometer-scale features it would be sufficient to fabricate quasi-3D structures consisting of a relatively small number (≪10) of overlapping patterns, provided that this can be realized without loss of pattern fidelity. For example, an active layer including top and bottom electrodes, such as a charge capacitor or a sensing device, consists of a stack of three layers. Including a buffer layer to shield the structure from the reactive SiO_x phase on the silicon substrate surface raises the total to four. In our model system the first layer was YSZO in all cases, and this was followed by up to four layers of $BaTiO_3$. The obtained stacks consisted of discrete lines, i.e,. no thin layer (residual layer) was observed between the lines.

EXPERIMENTAL SECTION

Preparation of Sols. A precursor solution for YSZO was prepared as follows: yttrium(III) nitrate hexahydrate (99.9 %, Alfa Aesar GmbH) was dissolved in 2-propanol (99.5 %, Sigma-Aldrich), resulting in a stock solution with a concentration of 1 mol/L. A mixture of zirconium(IV) n-propoxide (70 weight % in n-propanol, Alfa Aesar GmbH) and 2-methoxyethanol (99.3 %, Sigma-Aldrich) was refluxed for 2 h at 105 °C. The final concentration amounted 1 mol/L. To 1000 μl of this stock solution, 1000 μL of glacial acetic acid (Acros) and 87 μL of the yttrium nitrate stock solution were added and stirred vigorously for several minutes, resulting in a zirconium concentration of 0.479 mol/L and an yttrium concentration of 0.042 mol/L.

For the $BaTiO_3$ precursor solution, titanium(IV) isopropoxide (99.999 %, Sigma-Aldrich) was dissolved in 2-methoxyethanol, yielding a 1 mol/L stock solution of titanium(IV) methoxyethoxide. Glacial acetic acid was added to barium acetate (99 %, Sigma-Aldrich) and the mixture was refluxed for 12 h at 105 °C in order to remove traces of water and to

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dissolve the barium acetate. The barium concentration of the resulting stock solution was 1 mol/L. Before deposition, 1000 μL of the barium and 1000 μL of the titanium stock solution were mixed and 300 μL of water were added under vigorous stirring, resulting in 0.435 mol/L solution of barium titanate precursor with $[H_2O]$: [Ti] = 16.67. The obtained sol was usually stable for several days when kept in the refrigerator.

Micromolding Experiments. PDMS molds were made by casting Sylgard 184 liquid PDMS against relief patterned Si masters and curing at 40 °C. The pattern in the masters consisted of lines of 1.5 μm width and 1 μm depth. The solidified molds were cut to a size of 1 × 1 cm^2. Si (001) wafers with a native oxide layer were used as substrates for patterning immediately after cleaning them by snow-jetting and O_2 plasma etching. Snow jetting involves clamping a substrate onto a hot stage at 120 °C, followed by cleaning the substrate with a high-pressure jet of supercritical CO_2.

After a small droplet (approx. 10 μl) of the YSZO precursor solution had been placed on the substrate heated to 30 °C, a self-built device was used to press the PDMS mold onto the substrate such that the pressure at the Si-PDMS interface amounted approx. 0.8 bar. These values were chosen because they had led to good results in earlier experiments (9). The temperature was raised to 80 °C and held for 1 h before removing the mold. The sample was dried for 1 h in air at 80 °C and then placed in a preheated microwave furnace (approx. 650 °C). Within 1 min, the furnace temperature was raised to 850 °C and held for 30 min before letting the sample cool to room temperature. This procedure was repeated up to four times on one sample with $BaTiO_3$ precursor solution, every time with a different orientation of the line pattern.

Pattern Characterization. Scanning electron microscope (SEM) images were taken on a Zeiss LEO-1550. X-ray Diffraction (XRD) scans were carried out on a Philips diffractometer PW3020 with Cu K_α radiation. The atomic force microscope (AFM) was a Veeco Multimode.

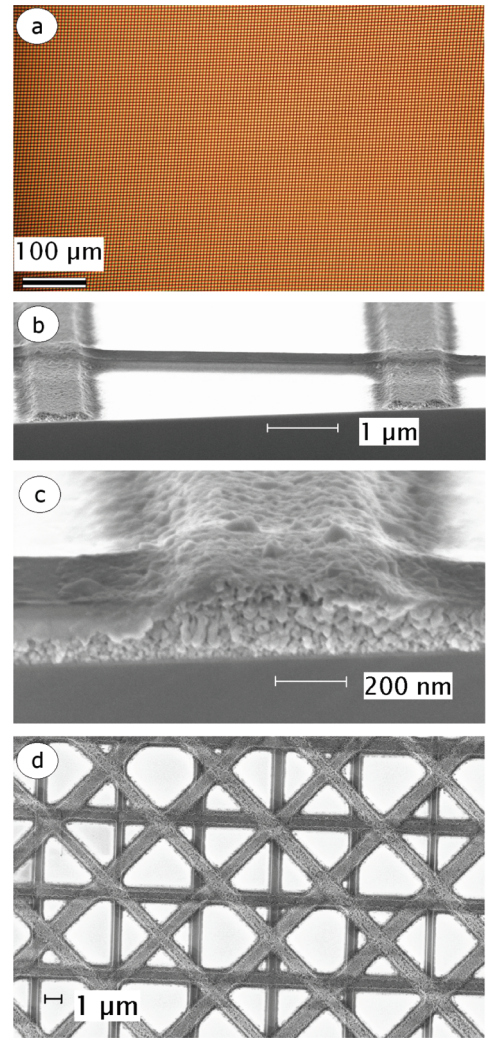

FIGURE 1. (a) Optical microscope image of a stack of YSZO lines (vertical direction) and $BaTiO_3$ lines (horizontal direction). (b) SEM image (SE, 2.0 kV) of a stack of YSZO lines (horizontal direction) and $BaTiO_3$ lines (vertical direction). (c) Magnified view of cross-section of $BaTiO_3$ and YSZO lines, showing the $BaTiO_3$ line to be coarse crystalline compared to the underlying YSZO phase. (d) SEM image (SE, 1.2 kV) of one YSZO layer (vertical lines) and three $BaTiO_3$ layers.

RESULTS AND DISCUSSION

Optical microscopy showed that the patterns were of homogenous thickness and quality over areas of several mm^2, see Figure 1a. Both scanning electron microscope (SEM) images of the samples' surfaces and mechanical scratch tests (10) revealed the absence of an unwanted residual oxide layer between the features, see Figure 1b. A SEM images of the sample's fracture faces at higher magnifications is shown in Figure 1c. Please note that the fracture surface through the sample intersects the junction of the two lines not in the centre but rather at the front edge of the junction, where the $BaTiO_3$ line is covering the upper part of the underlying YSZO. The SEM image reveals that both the YSZO and the $BaTiO_3$ are porous, and that the YSZO crystallites are smaller than the $BaTiO_3$ ones. Both the YSZO and $BaTiO_3$ lines show a thin outer layer of higher density than the interior. In the case of YSZO, this dense layer is very smooth, while the surface of the $BaTiO_3$ lines still reflects the large crystallite size and high porosity of the material underneath. The edge roughness of the line patterns is ~100 nm, about 8% of the total width of the lines.

Up to five patterned layers could be stacked on the substrate without any noticeable residue layer between the lines or cracking of lines. An example with 4 layers is shown in Figure 1d. Successive patterns were added relative to each other in such a manner that one to three stacked layers were present on various locations of the substrate. The atomic force microscopy (AFM) image in Figure 2a shows a multilayer pattern consisting of one YSZO and four $BaTiO_3$ line patterns. Cross-sectional profiles of three line sets, including the fifth layer, are shown in Figure 2b.

The data indicate that the lines are relatively homogenous in width, and layer heights vary between 155 and 185 nm. Considering the fact that microwave annealing at 850°C for 30 min was applied after each patterned layer, some lines have undergone a more extensive thermal annealing treatment than others, so that some variation between lines is indeed expected. The phase composition of a multilayer

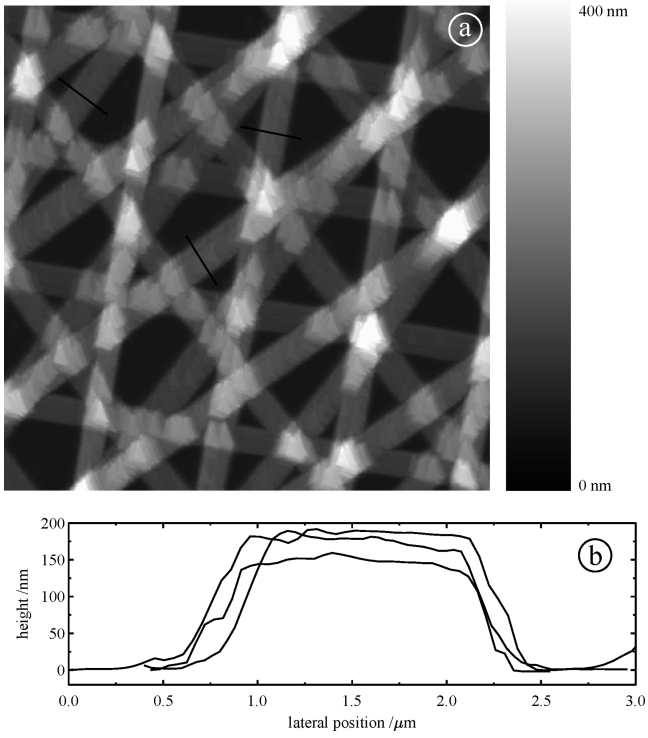

FIGURE 2. (a) AFM image (contact mode, 20×20 μm^2 scan size) of a stack of one patterned YSZO layer and four $BaTiO_3$ layers. (b) Cross-section height profiles were taken and plotted on three locations (indicated by black lines), showing that the YSZO and $BaTiO_3$ lines are uniform in width and height.

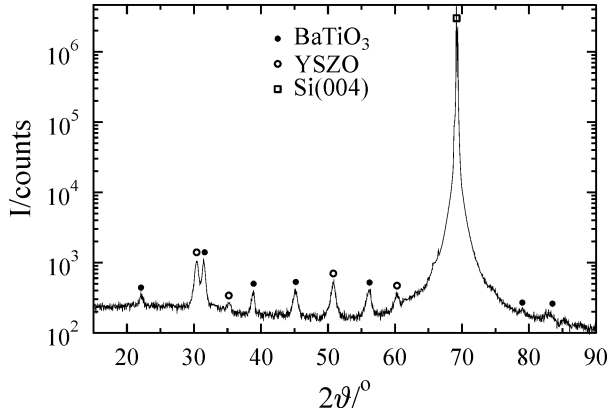

FIGURE 3. X-ray diffraction pattern of Si (001) substrate with YSZO and BTO multilayer micropatterns.

pattern on a silicon substrate was determined by x-ray diffraction. Only the YSZO and $BaTiO_3$ phases were found to be present as diffracting film components, see Figure 3.

When a sixth layer was added, the fidelity of the reproduced pattern was very low and residual material was observed between the lines and along the edges. For the given system with an aspect ratio of 0.10−0.13, the maximum number of stackable layers amounts thus five. Because sol−gel solutions typically have solids concentrations and viscosities of similar magnitude, the thicknesses and aspect ratios of other soft lithographically patterned oxides are typically in the same size range (1). The maximum stack number will therefore be similar when other comparable solutions are used. The number realised here is sufficient for most simple device architectures, as discussed above. By modifying other parameters in our process, e.g., changing the elastic modulus of the elastomeric mold, or adjusting the solids content, viscosity or surface tension of the sol−gels, it may be possible that multilayer patterns with more layers can be realized without changing the essence of the patterning procedure. The progress reported here is believed to form a step forward on the way to a versatile additive micropatterning technique with which simple multimaterial device structures could be fabricated in a reliable, fast, and cost-effective manner.

CONCLUSIONS

Stacks of line-patterned YSZO and $BaTiO_3$ films were obtained by combining oxide thin film growth from sol−gel precursors with micromolding, a common technique for patterning liquid films. The stacks consist of lines with sharp edges, forming well-defined corners. The work demonstrates a method to obtain multicomponent patterned thin films by applying a rather simple patterning technique requiring only basic lab equipment.

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