Nanostructure patterns of piezoelectric and ferroelectric complex oxides with various shapes, obtained by natural lithography and pulsed laser deposition

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Received 25 October 2005, in final form 22 February 2006
Published 24 April 2006

Abstract

A variety of patterns of well-ordered perovskite-type complex oxide nanostructures were obtained by pulsed laser deposition (PLD) on conductive single crystalline substrates through latex sphere monolayer and double-layer masks. Patterns obtained via deposition through hexagonally close packed (hcp) latex sphere monolayers include the usual arrays of hexagonally ordered nanoislands, hexagonal arrays of nanorings of much lower height coexisting with hexagonal nanoislands, hcp shell-like structures, and hexagonally interconnected nanocrown arrays. The formation of the nanopatterns depends on the ambient gas pressure during PLD, with well-separated nanoislands obtained at low pressures, and interconnected nanocrowns formed at high pressures. After annealing, the obtained BaTiO\textsubscript{3} and SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9} nanopatterns were examined by piezoresponse force microscopy using conductive scanning probes. Under an external biasing electric field, polarization domain reversal was observed in the nanopatterns with deep submicron lateral dimensions. BaTiO\textsubscript{3} nanocrowns ∼9 nm high are ferroelectric, while SrBi\textsubscript{2}Ta\textsubscript{2}O\textsubscript{9} nanorings of ∼5 nm thickness show at least piezoelectric activity. In addition to the patterns of hexagonally ordered nanostructure arrays, a pattern of rhombohedrally ordered nanostructure arrays was also fabricated by deposition through latex sphere double layers.

1. Introduction

Natural lithography \cite{1} or nanosphere lithography (NSL) \cite{2} is a template-based nanopatterning approach in which latex spheres are used to define lithographic masks for either deposition or etching. NSL is an inexpensive, versatile, technologically simple, and parallel technique, which can produce structures of nanometre dimensions with high throughput. In NSL, the spacing and size of the periodically arranged nanostructures can be readily controlled by using latex spheres with different diameters and/or changing the amount of material deposited. Some variants of NSL were developed to fabricate extended structures \cite{3} or complex morphologies \cite{4}.

Complex oxides are multifunctional materials with a variety of useful properties such as piezoelectricity, ferroelectricity, pyroelectricity, superconductivity and magnetoelectricity. Among these oxides, perovskite-type complex oxides showing piezoelectricity and ferroelectricity \cite{5} potentially have device applications such as non-volatile, ultrahigh-density memories \cite{6,7} and microelectromechanical systems (MEMS) \cite{8}. Patterns of nanostructured complex oxides will be of great interest in the field of nanoelectronics. Size effects on ferroelec-
Nanostructure patterns of piezoelectric and ferroelectric complex oxides

Pulsed laser deposition (PLD) [13] is a versatile thin film deposition technique. Using PLD through natural lithographic masks, we have recently prepared well-ordered arrays of complex oxide nanostructures [14–17] on conductive single crystalline SrTiO$_3$ substrates to explore the size effects in complex oxides for ferroelectric memory and MEMS applications. Due to the low melting point of the latex spheres, PLD of the ferroelectric oxides has to be carried out at room temperature, and post-deposition annealing is necessary to crystallize the as-prepared amorphous oxide structures. Nonetheless, we have demonstrated that (001)-oriented epitaxial ferroelectric BaTiO$_3$ nanostructures can be obtained using this approach, as shown by detailed cross-sectional transmission electron microscopy studies [15].

Our studies are aimed at exploring how downscaling influences the properties of ferroelectric oxide materials and at determining the critical size below which the structures lose piezoelectricity and ferroelectricity. It should be mentioned that, in the present work, the nanostructure patterns are fabricated on conductive single crystalline substrates. With the conductive substrates used as bottom electrodes, and contacting SPM probes with conductive coatings as top electrodes, individual complex oxide nanostructures in the patterns under investigation are actually sandwiched in between to form sub-100 nm thick capacitor structures having deep submicron lateral dimensions. In this paper, we show that a variety of patterns of complex oxide nanostructures can be obtained by PLD using natural lithographic masks. We have investigated the nanopatterns using PFM and furthermore demonstrated polarization domain switching in the nanopatterns.

2. Experiments

Latex sphere templates were prepared on conductive Nb-doped SrTiO$_3$ single crystalline substrates (0.5 wt% of Nb) by spin coating. Commercial water solutions of monodisperse polystyrene latex spheres of 1 μm in size were used. Both monolayers and double layers were found in the latex sphere templates made using this approach, with hcp monolayers predominating.

The latex sphere templates were used as PLD masks. The deposition was carried out at room temperature in a chamber with a base pressure of 1 × 10$^{-9}$ Torr using a KrF excimer laser (248 nm wavelength) with an energy of 400 mJ and a repetition rate of 1 Hz. Commercial BaTiO$_3$ and SrBi$_2$Ta$_2$O$_9$ ceramic targets were chosen for the PLD. BaTiO$_3$ and SrBi$_2$Ta$_2$O$_9$ nanopatterns were prepared on (100)- and (111)-oriented conductive SrTiO$_3$ single crystalline substrates, respectively. Pure oxygen was used as the background gas, and the chamber pressure was changed to investigate its effect on the formation of the nanostructure patterns. The typical deposition time was 10 min. After deposition the latex spheres were removed using methylene chloride, and the pattern left on the substrate was then annealed in air to form crystalline nanostructures.

The morphology of the obtained nanopatterns was examined using a JSM-6300F scanning electron microscope. The topography of the nanopatterns was examined using a Dimension 5000 atomic force microscope from Digital Instruments. Tapping mode atomic force microscopy (AFM) images were obtained using a standard silicon cantilever with a tip radius of less than 10 nm. The experimental setup used for the nanoscale piezoelectric investigations consists of a commercial scanning probe microscope, an ac voltage source, a lock-in amplifier, and a dc voltage supply. The scanning probe microscope was set in contact mode at a constant force. For piezoelectric imaging, a commercial silicon cantilever with a W$_x$C conductive coating and a typical force constant $k = 2$ N m$^{-1}$ was used (frequency 18.87 kHz; amplitude 1 V). To investigate polarization domain switching and measure piezoresponse hysteresis loops by PFM, dc biasing voltages were applied to the nanostructures via a commercial TiN-coated silicon cantilever with a typical tip radius less than 35 nm and a typical force constant $k = 40$ N m$^{-1}$ (frequency 16.52 kHz; amplitude 1 V).

3. Results

3.1. Hexagonally ordered nanoisland arrays

Figure 1 presents scanning electron microscopy (SEM) images of a 1 μm diameter hexagonally close packed latex sphere monolayer mask on a conductive single crystalline substrate. In figure 1(b) pores are found in the monolayer, clearly showing boundaries between the latex spheres and the bare substrate.

Hexagonal arrays of nanospheres are the usually observed nanopatterns obtained using NSL. Ferroelectricity in such hexagonal nanopatterns involving complex oxides has been reported earlier [14–16]. Figure 2 shows SEM images of patterns of hexagonal arrays of SrBi$_2$Ta$_2$O$_9$ nanospheres after annealing. The hexagonal nanosphere array was formed by the ablated species directly reaching the substrate, passing the interstices between the latex spheres of the monolayer mask. As can be seen in figure 2(a), besides the nanostructure arrays, laterally extended structures and large islands with lateral dimensions of a few microns—all with nanometre-range thickness—were also fabricated, which are due to deposition through stacking defects (or low-angle boundaries) and pores within the latex sphere templates, respectively, as shown in figure 1.

3.2. Hexagonally close packed shell-like structures

When using natural lithographic masks for PLD of complex oxide nanostructures, the laser plume is not only projected through the interstices between the latex spheres, but it also reaches the surface of the latex spheres, covering them and thus forming shell-like structures. Usually when the latex spheres were detached from the substrates, the shell structures went away with those spheres. Sometimes, however, when the latex spheres were not fully removed, after annealing the shell structures were left on the substrates. Figure 3 displays shell
Figure 1. Latex sphere (1 µm diameter) template used as a mask for the pulsed laser deposition: (a) continuous monolayer, and (b) part of a monolayer with pores.

Figure 2. SrBi$_2$Ta$_2$O$_9$ nanoislands after annealing: (a) low-magnification image showing large-area hexagonal arrays with laterally extended structures visible in the low-angle boundary regions; (b) close-up view of a well-ordered hexagonal array.

Figure 3. Shell-like structures of SrBi$_2$Ta$_2$O$_9$ formed when latex spheres were not fully detached from the substrate before annealing: (a) low-magnification image showing an ordered shell structure array coexisting with the usual hexagonal nanoisland array; (b) medium-magnification image of the hcp shell structures; (c) close-up view showing a triangular-shaped nanostructure present at the interstice of the three adjoining shell structures; (d) high-magnification image showing that some shell structures at the edge of the arrays were distorted.

structures formed during PLD of SrBi$_2$Ta$_2$O$_9$. Figure 3(a) is an image showing the ordered shell structure arrays coexisting with the hexagonal nanoisland arrays. Figure 3(b) is a magnified image of the hcp shell structures. Figure 3(c) is a close-up view of the shell structures showing the presence of a triangular-shaped nanostructure at the interstice of the three adjoining shell structures (see white arrow). Distorted shells as can be seen at the edge of the array in figures 3(a) and (d) indicate that these structures are indeed hollow shells. The shell arrays on the substrate cannot be latex sphere residues.
Nanostructure patterns of piezoelectric and ferroelectric complex oxides

simply because those specimens have been subjected to an annealing treatment at 650 °C in air for 2 h. Based upon the deposition rate used, the thickness of the obtained shell structures should be well below 100 nm.

3.3. Rhombohedrally ordered nanoisland arrays

Apart from the usual hexagonally ordered nanoisland arrays due to deposition through the latex sphere monolayer masks, nanostructure arrays with a new rhombohedral ordering were fabricated by deposition through latex sphere double layers. Rhombohedrally ordered nanostructure arrays obtained by PLD of BaTiO$_3$ through a double-layer mask are shown in figure 4(a). Figure 4(b) shows the presence of both a monolayer and a double layer within a latex sphere mask, with the bare substrate visible at a large pore within the monolayer. By comparing the high-magnification images of figures 4(c) and (d), it is clearly shown that the nanostructure arrays with rhombohedral ordering have a larger spacing but considerably smaller lateral dimensions than the usual hexagonally ordered nanostructure arrays. Compared to the monolayer situation, the PLD-ablated species have to travel further when passing through the narrow interstices within the double layer before finally ending at the surfaces of the substrates underneath.

3.4. Patterns of coexisting nanorings and nanoislands with a hexagonal ordering

Under certain conditions, ring-like nanostructures were discovered after removal of the latex sphere masks, and they were found to coexist with the pyramid-shaped nanoislands. Such nanoring structures are much thinner than the nanopyramids (∼5 nm high in the present work), with an average diameter of ∼0.4 µm and an estimated width of ∼100 nm. After annealing, in some cases such nanorings cannot be visualized anymore, while in other cases the nanorings simply break into several pieces. Figure 5(a) is a side view, and figure 5(b) a topographic top view, of an as-prepared SrBi$_2$Ta$_2$O$_9$ nanopattern prior to annealing; an array of nanoring structures with hexagonal ordering is clearly seen to coexist with the well-ordered hexagonal array of nanopyramids. Annealed arrays of mixed nanorings and nanopyramids were investigated using conductive scanning probes. A PFM image (figure 5(c)) of the pattern reveals that the nanorings are not artefacts due to latex sphere residues. Rather they are nanoring structures of complex oxides caused by accumulation of pulsed laser ablated species around the contact zone between the latex spheres and the underlying substrates.

3.5. Patterns of interconnected hexagonal nanocrowns

All the aforementioned nanopatterns were formed at high vacuum, i.e. at low ambient gas pressures (1 × 10$^{-6}$ Torr) during PLD. At high ambient gas pressures, it has been discovered that patterns of hexagonally interconnected nanocrowns can be obtained [17]. Figure 6 shows a nanocrown pattern obtained at an ambient gas pressure of 1 × 10$^{-2}$ Torr during PLD of BaTiO$_3$. As shown in the tapping mode AFM side view of the nanocrown pattern prior to annealing, nanoring structures are again visible, and they are found to coexist with the nanocrown pattern but to have much lower height. Figure 6(b) and figure 6(c) are a typical topographic image and a PFM image, respectively, of the ∼9 nm high patterns of hexagonally interconnected BaTiO$_3$ nanocrowns after annealing. It is noted that the above-mentioned nanoring structures become invisible after annealing. Piezoelectric response hysteresis loops (not shown here; see [17]) were also obtained from the nanocrown pattern, demonstrating ferroelectricity in the ultrathin nanocrowns of only ∼9 nm height.
Figure 5. Nanoring structures: (a) tapping-mode AFM side view of an as-prepared SrBi₂Ta₂O₉ nanopattern prior to annealing, showing the presence of ring structures within the nanopyramid arrays with usual hexagonal ordering; (b) contact-mode topographic image and (c) PFM image. In (c) the annealed nanopattern (3 µm × 3 µm) was examined using SPM operated in piezoelectric mode, proving that the nanorings are not artefacts.

At high ambient gas pressures, the growth rate is most probably reduced by the higher probability of the laser-ablated species being scattered by background gas molecules. In this case, part of the laser-ablated species is being spread to the surrounding regions rather than projecting directly at the interstice sites, thus leading to the formation of an interconnected hexagonal nanocrown pattern.

4. Discussion

Compared to previous NSL studies, the present work resulted in a number of advances. First, natural lithography has been used for the nanopatterning of complex oxide structures on substrates, whereas so far the NSL approach has been mainly used for metals [1, 2, 18, 19] or simple oxides such as TiO₂ [20]. Second, we have used PLD (while most of the other investigations used thermal evaporation), which enabled us to use the ambient gas and its pressure variation to modify the type (shape) of the nanopatterns, in particular obtaining novel nanocrown patterns at high ambient gas pressure. Third, the formation of functional complex oxide nanoring structures has been observed. An early NSL paper reported the observation of similar ring structures [18] to coexist with hexagonal arrays of metal nanodots, showing corresponding topography images. In the present work, however, we have simultaneously recorded PFM images of the nanoring structures. Finally, in addition to well-ordered nanostructure arrays of the usual hexagonal ordering, we have confirmed—now for complex oxide systems—an early finding in metal systems [2] according to which nanostructure arrays of a new rhombohedral ordering can be produced using double-layer masks. In addition, we have fabricated patterns of shell-like nanostructure arrays of complex oxides; a similar finding was reported earlier in metal systems [21] using sputtering.

The present nanoscale PFM investigations using conductive scanning probes, and former measurements of piezoresponse hysteresis loops, confirm that for the various nanopatterns obtained, 26 nm high BaTiO₃ [15] and 30 nm high SrBi₂Ta₂O₉ [16] nanopyramids, and 9 nm high BaTiO₃ nanocrows [17] are still ferroelectric. In this paper, we have shown that the ~5 nm high SrBi₂Ta₂O₉ nanorings are piezoelectrically active. Further investigations of possible ferroelectric switching of the nanorings, and piezoelectric investigations of the obtained shell-like structures are rather complex and will be a challenging task for future investigations.

To further demonstrate ferroelectricity in the obtained nanostructures, the observation of polarization reversal is presented in figure 7. Figure 7(a) is a contact mode AFM topographic image of a BaTiO₃ hexagonal nanopattern with a height of about 44 nm. As shown in the PFM images of figures 7(b) and (c), initially the as-prepared BaTiO₃ nanopattern exhibited a downward polarization or negative domain state, visualized by the dark contrast. When a positive dc bias of 10 V was applied, the downward polarization domains in the nanopattern switched to the opposite direction,
as shown by the bright contrast corresponding to a positive domain state with upward polarization (figure 7(c)).

This paper has focused on a variety of nanopatterns fabricated by combining natural lithography with PLD. All the nanostructures presented were obtained using templates consisting of 1 µm latex spheres. However, it should be noted that natural lithography has a potential of further downscaling the obtained nanostructures. The lateral dimensions can be decreased using templates consisting of smaller latex spheres, and the height can be reduced by a decrease in deposition time. For example, our previous work has demonstrated that the lateral dimensions of the nanoislands can be reduced to ∼160 nm [15] when masks of 0.5 µm latex spheres are used. Apart from the well-ordered nanopatterns, extended mesoscopic structures were generated due to deposition through the stacking defect sites or pores present in the latex sphere masks, which can be used as a reference for the investigation of the size effect on piezoelectricity and ferroelectricity.

5. Conclusions

Natural lithography was used to define a lift-off-type deposition mask for the fabrication of well-ordered arrays of nanostructures of complex oxides such as BaTiO3 and SrBi2Ta2O9 on conductive Nb-doped SrTiO3 single crystalline substrates. The nanopatterns obtained via PLD through the hcp latex sphere monolayer masks include hexagonal arrays of pyramid-shaped nanoislands, ordered nanoring structures in coexistence with the hexagonal nanopyramid arrays, hcp shell structure arrays, and interconnected hexagonal nanocrown patterns. Piezoresponse force microscopy images were recorded from the obtained ferroelectric nanopatterns, and polarization domain switching was observed under external electric field. PLD through double-layer masks leads to ordered nanostructure arrays with a rhombohedral ordering.

Acknowledgment

WM is grateful to the Alexander von Humboldt Foundation for financial support.

References