Applied Surface Science 256 (2010) 4777–4783

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Nanoscale patterning of functional perovskite-type complex oxides by pulsed laser deposition through a nanostencil

Cristian-Victor Cojocaru [1], Riad Nechache, Catalin Harnagea, Alain Pignolet *, Federico Rosei *

INRS – Énergie, Matériaux et Télécommunications, Université du Québec, 1650 Boulevard Lionel-Boulet, Varennes, QC J3X 1S2, Canada

ARTICLE INFO

Article history:
Available online 4 February 2010

Keywords:
Parallel patterning
Nanostencil lithography
Pulsed laser deposition (PLD)
Perovskite complex oxides
Ferroelectric nanostructures
Barium titanate

ABSTRACT

We present studies on parallel nanoscale patterning of piezoelectrics/ferroelectrics via deposition through a nanostencil. Unlike other processes reported for oxide nanostructuring, we selectively deposit the material, directly, by interposing a nanosieve between the substrate and the deposition source. We show that this selective deposition can be realized even with materials as complex as perovskite oxides, both at room temperature and at high temperature. We elaborate on and analyze the performance of the nanostenciling approach for the growth of barium titanate $BaTiO_3$ on strontium titanate $SrTiO_3$(1 0 0). The patterned structures of ferroelectric materials are characterized by X-ray diffraction and imaged locally by scanning probe microscopy in piezoresponse mode to individually probe their functionality.

1. Introduction

Following the trend of the semiconductor industry with respect to the continuing miniaturization of integrated devices, functional oxide ceramic thin films are experiencing a similar evolution from microtechnology towards nanotechnology. Increasing efforts are undertaken to nanostructure and pattern thin films of functional oxides and several recent reviews have debated the advantages and difficulties associated with either the top-down or the bottom-up approaches to pattern electroceramic thin films [1–5]. Although some of the alternative patterning techniques to photolithography have already demonstrated the potential to deliver structures with smallest features close to 100 nm, their integration within a more general and complex fabrication scheme is very challenging. The requirement of perfect registration is unavoidable for a process to be used in future micro- or nano-electronics.

As structure dimensions become progressively smaller, the new functional materials being envisioned often exhibit pronounced size effects which represent a significant deviation of the properties of low-dimensional structures with respect to their bulk properties [6,7]. The "size effect" in ferroelectrics, induced by a reduction in geometrical dimensions, has been shown to result, among other phenomena, in a reduced remnant polarization and dielectric permittivity, in changes in the domain structure, a decrease of the phase transition temperature and an increase of the coercive field [8]. Fundamental studies of patterned functional oxide ceramics are further required for these new materials, especially in the nanoscale regime. These studies are crucial to establish experimentally the useful critical size for each material, i.e. the smallest size at which it would still provide the desired functionality [9–15]. In the particular case of ferroelectric materials, theoretical predictions suggest that, due to an increasing role of the depolarization field and the weakening of long range cooperative interactions, which are the driving force for ferroelectricity, the latter is supposed to disappear below a critical size. These calculations suggest a material-dependent critical thickness and correlation volume (e.g. 2.4 nm for a $BaTiO_3$ thin film between two metallic $SrRuO_3$ electrodes) [16]. Other theoretical studies on size effects estimated the minimum volume at which the polarization and the ferroelectric properties should vanish (critical volume) to be about 1000 nm^3 [17]. Experimental studies demonstrated that ferroelectricity exists in ultrathin (4 nm) $Pb(Zr,Ti)O_3$ (PZT) epitaxial films [18] and ferroelectricity was observed in $BaTiO_3$ (BTO) films about 5 nm thick [19]. Such size effects in general are poorly understood.

The top-down methods that are currently used in nanotechnology provide high-precision positioning and size control yet are often limited in resolution or are not suitable for complex oxide materials. For example, a conventional patterning process, based on usual resist lithography followed by etching of the oxide film is fraught with severe problems, when applied to ferroelectric thin films: contamination and side-wall redeposition can alter the polarization switching (even for features as large as micrometers) and constitutes challenging issues to be overcome in the patterning of complex oxides in general and of ferroelectric thin

* Corresponding authors.
E-mail addresses: pignolet@emt.inrs.ca (A. Pignolet), rosei@emt.inrs.ca (F. Rosei).
[1] Present address: NRC-Industrial Materials Institute, Boucherville, QC, Canada.

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.01.103

films in particular. Alternatively, bottom-up strategies, either by physical or chemical self-patterning of complex oxides [20,21] hold the promise of realizing much smaller features than those achievable with top-down techniques. Self-assembly governed by growth mechanisms similar to those found for Ge islanding on Si(0 0 1) surfaces [22], overcome the low throughput and processing damage of conventional patterning methods [12]. Nevertheless, they suffer from poor registration and to achieve a certain organization requires prior substrate patterning, which in turn involves an additional top-down processing step [23]. Though appealing for scientific purposes, bottom-up approaches are presently still ineffective, somewhat unreliable and not yet ripe to be implemented as new technologies.

We present here studies on parallel nanostructuring and patterning of ferroic oxides, mainly piezoelectrics/ferroelectrics, via pulsed laser deposition (PLD) through a nanostencil. The original aim was to assess whether nanostenciling can become a general-purpose nanoscale patterning technique that offers both high resolution and unique flexibility for any combination of deposited material/substrate. Unlike most of the other techniques reported for oxide nanostructuring, we do not process or modify the substrate, but selectively deposit the material, directly, by interposing the nanosieve between the substrate and the deposition source. Simultaneously, there is an inherent control of the locations where the nucleation starts and where the structures' growth will further take place, if the stencil is accurately positioned with respect to the substrate. A direct copy of the apertures opened in the stencil is realized on the substrate by "forcing" the material to pass through the former providing thus a technique for parallel fabrication of ordered arrays of islands. A similar approach has been investigated independently by other groups [24–26]. In particular, we compare patterns of $BaTiO_3$ (a compound less sensitive to variations in by depositing parameters) obtained by both room temperature deposition (and crystallized by subsequent annealing) and by depositing at high temperature. The patterned structures of ferroelectric materials are characterized by X-ray diffraction (XRD) and probed locally by scanning force microscopy in piezoresponse mode for ferroelectricity.

2. Experimental

PLD patterning experiments were conducted using laser interference lithography (LIL)-based stencil masks, with built-in 500 nm thick Si_3N_4 nanosieves with circular apertures. These stencils have hexagonal arrays of pores (350 nm in diameter) with a periodicity of either 1.6 μm or 700 nm and are patterned on 12–14 free-standing, low stress (LS-SiN) membranes (2 mm in length and 100 μm in width each, 100 μm apart). The Si_3N_4 membranes are prepared on single crystal Si(1 0 0) wafers 380 μm thick and the stencil's dimension is 5 mm × 5 mm with an active area of ~2 mm × 2.7 mm. The stencils were mechanically clamped and temporarily fixed onto Nb-doped (1 0 0)-oriented $SrTiO_3$ substrates. The assembly substrate-stencil was mounted in the vacuum chamber of a PLD system, in front of a dense $BaTiO_3$ stoichiometric ceramic rotating target. A KrF Lumonics PM-800 excimer laser (radiation with λ = 248 nm, pulse duration = 15.4 ns) was employed for ablation with a 45° incidence angle on the target and a laser fluence of 2 J/cm^2. A set of depositions were carried out at room temperature (RT), in vacuum at 1×10^{-5} mbar (7.5×10^{-3} mTorr), with a laser repetition rate ranging from 5 to 10 Hz and a target–substrate distance of 6.5–7 cm. We further pursued the nanostenciling of $BaTiO_3$ directly at high temperature, in low O_2 background gas conditions according to the parameters provided in Table 1. This was possible only thanks to the high thermal resistance and stability of the Si_3N_4 membranes at temperatures up to 800 °C.

Table 1
Deposition conditions for the patterns analyzed in this work.

ID	Temperature	Pressure [O_2] (mTorr)	Post-deposition annealing
BTO pattern I	620 °C	7.5×10^{-3}	N/A
BTO pattern II	620 °C	10	N/A
BTO pattern III	RT	7.5×10^{-3}	RTA–700 °C

All the samples were prepared on $SrTiO_3$ single crystalline substrates (0 0 1)-oriented, using the same number of laser ablation pulses (N = 5000) and stencils with the same aperture diameter (350 nm). Two samples were fabricated with stencils having periodic apertures spaced with 1.6 μm pitch. After deposition the samples were cooled down to room temperature, naturally, in a 150 mTorr O_2 background pressure. Once the deposition was completed the stencils were unclamped and simply "lifted off" (separated) from the substrate. The properties of a continuous epitaxial film (~100 nm thick) deposited in high O_2 atmosphere were also investigated.

X-ray diffraction in grazing incidence (GIXRD) and Bragg–Brentano (θ–2θ) configuration was used to investigate the crystalline phases present in the patterned structures and their quality. The lattice parameters of the epitaxially patterned samples were studied more in detail by X-ray reciprocal space mapping (RSM), a technique typically used in epitaxial films to determine the strain state in thin films.

Local ferroelectric testing was performed using Piezoresponse Force Microscopy (PFM) as described earlier [27]. We applied a small AC voltage (typically 0.5 V at 29 kHz) between the conductive AFM tip and the sample bottom electrode. Hysteresis loops were acquired by positioning the AFM tip over the center of an individual nanostructure, then the local piezoresponse signal was recorded while a superimposed DC bias voltage was swept between −10 V and +10 V. The induced local mechanical displacement was detected, using long integration times for the lock-in amplifier connected to the AFM. The out-of-plane piezoelectric coefficient d_{33} was calibrated according to the procedure developed by Harnagea and Pignolet [28].

3. Results and discussion

3.1. Stencil lifetime

Rapid and parallel fabrication of ordered BTO nanostructures was achieved at RT in a single deposition step, over the whole sieve areas. Fig. 1(a) displays an SEM micrograph detail from a LS-Si_3N_4 nanosieve with pores of 350 nm in diameter and a 700 nm pitch used during the depositions and Fig. 1(b) shows the well-ordered, dome-shaped, as-deposited structures, obtained via stenciling through the latter.

The SEM micrograph in Fig. 1(c) reveals structures with base enlarged to 385–390 nm and thus suggesting an overall base broadening of ~35–40 nm, i.e. ~10% larger than the nominal value of the apertures. We found that, for the sieves with 350 nm diameter circular holes, the transfer efficiency (defined as the ratio between the height of the structures and the thickness of a film deposited in the same conditions) is above 80%.

Subsequent depositions using the same stencils revealed that for a total, nominal thickness of the deposited BTO equivalent to 3.5 times the aperture diameter, the lateral size of the replicated structures shrank by 30% (Fig. 1(d)).

The choice of the physical vapor deposition technique used in combination with nanostenciling plays an important role and the control of the interaction of the material to be deposited, with the membrane apertures, remains a matter of further examination. Identifying efficient cleaning recipes for the stencils, such as