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Citation: Applied Physics Letters **87**, 113114 (2005); doi: 10.1063/1.2048818

View online: http://dx.doi.org/10.1063/1.2048818

View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/87/11?ver=pdfcov

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Patterning of ferroelectric nanodot arrays using a silicon nitride shadow mask

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(Received 11 May 2005; accepted 25 July 2005; published online 9 September 2005)

We grew well-ordered arrays of ferroelectric $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) nanodots on a $SrRuO_3/SrTiO_3$ substrate by pulsed laser deposition. A silicon nitride shadow mask with ordered holes was used for patterning of the PZT arrays. Each dot has a height of ~15 nm and a diameter of ~120 nm with a similar dome shape over a large area. The ferroelectric properties of individual PZT dots were investigated by piezoresponse force microscopy. A single dot could be polarized individually and the polarized state remained unrelaxed to ~20 min. © *2005 American Institute of Physics*.
[DOI: 10.1063/1.2048818]

Ferroelectric materials have drawn considerable interest due to their wide applications in sensors, actuators and nonvolatile memories.[1,2] Recently, there have been suggestions that one may use arrays of submicron ferroelectric cell for mass-storage applications instead of magnetic media in a high density disk driver.[2–6] For these applications, they should be patterned to submicron scale (now sub 100 nm) in order to increase the capacity of an integrated chip. In submicron dots, fatigue, inhomogeneity of imprint and switching, easy relaxation and low temperature processing have been major issues to be resolved.[3–5,7–13] As these dots get even smaller, easy relaxation of a single domain nanodot and the superparaelectric effect[11] have become new problems to be understood. Technically, a new patterning method is demanded for good regularity, good crystallinity and low-budget processing of the dots. In this study, we report on how we achieved this goal by pulsed laser deposition (PLD) through a shadow mask of Si_3N_4.

There are various top-down and bottom-up methods in patterning small structures of ferroelectric materials. Granpule *et al.*[3,4] fabricated ferroelectric capacitors of $Pb(Nb_{0.04},Zr_{0.28},Ti_{0.68})O_3$ (PNZT) and $SrBi_2Ta_2O_9$ (SBT), with lateral sizes of 1 μm to sub-100 nm by focused ion beam milling. Alexe *et al.*[7] patterned ferroelectric memory cells of $Pb(Zr_{0.7},Ti_{0.3})O_3$ (PZT) and SBT with lateral sizes down to 100 nm by electron-beam direct writing. The nanoimprint lithography,[8] and the nanosphere lithography method[9] were also successful in fabrication of ferroelectric cells with submicron lateral size. In cases of bottom-up approaches, much smaller lateral sizes of a few nanometers could be obtained, though regular arrays are yet to be attainable.[10–12]

Shadow mask deposition has been an alternative method for nanoscale patterning.[14–17] So far, most materials were deposited by evaporation when shadow masks were employed, followed by high temperature annealing. It limits the use of photoresist solely for the lift-off process, and requires a direct etching process instead of shadow mask deposition.[5] The use of a shadow mask, compatible to high temperature processing, can resolve this problem. This method is free of damage from ion milling and could be applicable to *in situ* deposition since it avoids any possible contamination in dot formation. In addition, we could change the shape or size of the patterns if necessary. Recently, Lee *et al.*[13] have patterned La-doped $Bi_4Ti_3O_{12}$ (BLT) nanodot arrays by PLD using a gold nanotube membrane, which is a porous alumina-based mask. The deposition was carried out at room temperature, followed by postannealing to crystallize it. A Si_3N_4 membrane, which was used in the present study, can stand up to even higher temperature processing. More complex patterning is possible with a Si_3N_4 membrane, compared to a porous alumina mask.

We fabricated several Si_3N_4 stencil masks to define nanodot arrays. A 100-nm-thick Si_3N_4 was grown on an *n*-type Si (110) wafer. Then arrays of windows (500 $\mu m \times 50$ μm) were defined on the reverse side of the Si wafer with photolithography and reactive-ion-etch (RIE) process. The window patterns were transferred to Si wafer with wet-etch process in KOH (40 wt %, 90 °C). Using e-beam lithography and RIE process, the pore arrays of 100-nm-diam and 200 nm spacing were patterned onto a Si_3N_4 layer.

A $10 \times 10 \times 0.5$ mm $SrTiO_3$ (001) single crystal was used for the substrate. First, we deposited 100-nm-thick $SrRuO_3$ film, for the bottom electrode. Then, the silicon nitride shadow mask was attached to the substrate and fixed by clips, followed by $Pb(Zr_{0.2},Ti_{0.8})O_3$ deposition. The $SrRuO_3$ films and PZT nanodots were deposited by PLD method with the use of KrF excimer laser ($\lambda = 248$ nm), operating at a repetition rate of 10 Hz. The base pressure of the chamber was kept at 5.0×10^{-6} Torr. The substrate temperatures and oxygen pressures during deposition of $SrRuO_3$ and PZT were 760 °C, 300 mTorr and 660 °C, 100 mTorr, respectively. The energy intensities of laser were 2.36 and 2.68 J/cm^2. After deposition of the patterned PZT, it was postannealed at 660 °C for 30 min at 760 Torr of oxygen to avoid oxygen deficiency. Finally the nanodot arrays were obtained by just lifting off the shadow mask. The patterned structures were investigated by scanning force microscopy and their ferroelectric properties were studied by piezoresponse mode. In

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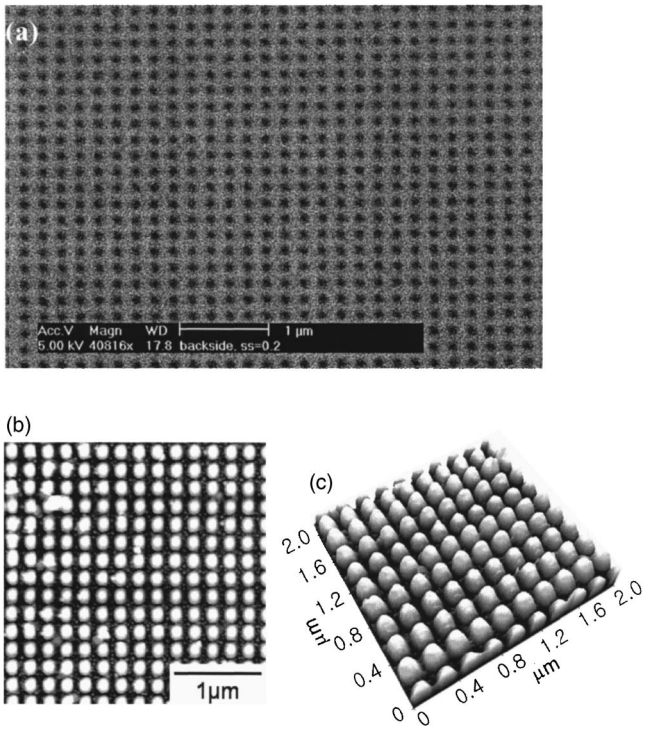

FIG. 1. (a) SEM image of a silicon nitride shadow mask. (b) and (c) Topographic images of PZT nanodot arrays.

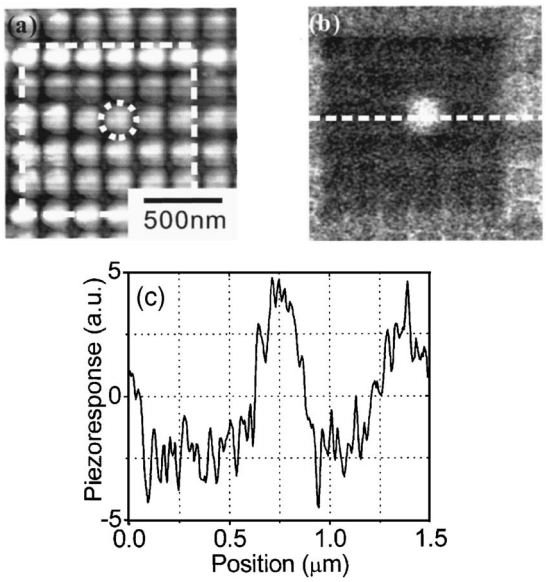

FIG. 2. (a) Topographic and (b) piezoresponse images of PZT nanodots. The 1×1 μm^2 region, marked in (a), and marked single dots were polarized with sample biases of −5 and 5 V. (c) Piezoresponse profile along the line marked in (b).

piezoresponse mode, ac modulation voltage of 2 V was applied between the conductive tip and the bottom electrode at a frequency of 76.5 kHz in contact mode.

Figure 1(a) is a scanning electron microscope (SEM) image of a silicon nitride membrane with 100 nm holes. The thickness of the membrane was about 100 nm. The patterned PZT nanodot arrays are shown in Figs. 1(b) and 1(c). The lateral size of the dot was about 120 nm and the height was about 15–20 nm. The inter-dot distance of PZT dot arrays was about 200 nm, exactly the same as the pore-to-pore distance of the shadow mask. Each dot was fully arranged and well isolated having a regular shape after deposition. It corresponds to the 2.5 Gbits/cm^2 in areal density.

The local switching of a single dot was examined using piezoresponse force microscopy (PFM). We applied a sample bias of −5 V to the 1×1 μm^2. Then a single dot was polarized positively by a sample bias of +5 V [Fig. 2(a)]. When we applied a higher voltage above 5 V, the patterns were damaged due to the high electric field. (A higher electrostatic energy is stored than in a planar film; therefore dielectric breakdown occurs at lower voltages than in a planar film.) Figure 2(b) is the piezoresponse image that shows the single dot is positively polarized among the negatively polarized dots. Their ferroelectric properties in terms of ferroelectric switching are clearly shown. From the piezoresponse signal, we could observe that the absolute piezoresponse value of the positively polarized dot is 28.3% larger than that of the negatively polarized background [Fig. 2(c)]. The asymmetry in electrodes (bottom electrode and tip) or internal field might result in this behavior. However, we could not observe any noticeable inhomogeneity such as an inversion of the center region after polarization.[6,18]

Our PZT nanodots had experienced no damage during patterning, and it was expected that each dot would be under a homogeneous strain state due to its small dimension. Therefore, there were less possibilities of domain pinning or strain inhomogeneity. Figure 3 shows the difference in piezoresponse signal between positively and negatively polarized dots as a function of time. The polarized states were maintained at 61.3% of their initial value after ~20 min. However, the polarization suddenly relaxed back almost to the original noise level after 30 min. The domain relaxation process is composed of nucleation and growth process. Once the relaxed region is nucleated, it grows by domain wall movement until it reaches a thermodynamically metastable state (domain wall pinning or faceting).[19] In patterned ferroelectrics, the domain wall could not propagate to neighboring dots in this way. Therefore, the patterned structures have an advantage of hindering growth stage on retention problems. The driving force of reversed nucleation is mainly due to its internal field or depolarization field.[19] Our patterned PZT dots were too thin in this respect. A sudden drop of polarization implies that the relaxation of polarized states is mainly related to the nucleation stage in our studies. If much thicker dots were patterned or a protected cap was co-deposited around the ferroelectric dot, an increased retention time could be realized. The detailed mechanism of retention characteristics of patterned PZT with size effect will be discussed elsewhere.[20]

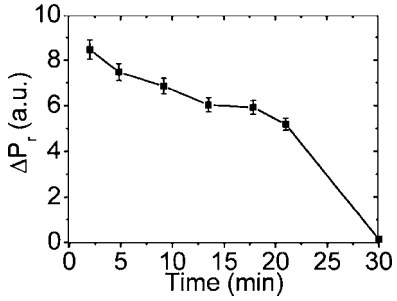

FIG. 3. Difference in piezoresponse signal between positively and negatively polarized dots as a function of time.

In conclusion, we have produced well-ordered PZT nanodot arrays with a silicon nitride shadow mask. We were able to deposit patterned PZT at a high temperature by PLD using a shadow mask. The ferroelectric switching of patterned arrays was probed by PFM. The polarization of individual dots was possible, and it was stable up to 21 min after polarization.

The authors thank K. Char for use of KrF laser source. This work was supported by the Korean Science and Engineering Foundation through the National Creative Research Initiatives Program.

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