Well-ordered arrays of pyramid-shaped ferroelectric BaTiO$_3$ nanostructures

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Monolayers of monodisperse latex spheres of micron size were used as deposition masks to fabricate arrays of ferroelectric nanostructures by pulsed laser deposition using a BaTiO$_3$ target. First, arrays of well-ordered structures were prepared on SrTiO$_3$:Nb (100) single-crystal substrates at room temperature. Investigations of these isolated as-deposited nanostructures by atomic force microscopy revealed that they have a pyramid-like shape with about 200 nm lateral size at half their height and form a regular hexagonal pattern. Then postdeposition annealing was used to crystallize the nanostructures. The ferroelectric properties of the crystalline structures were investigated by scanning force microscopy in piezoresponse mode. Piezoelectric hysteresis loops were recorded, demonstrating that the barium titanate nanopyramids have a remanent polarization and are switchable by an electric field, i.e., they are indeed ferroelectric. © 2003 American Institute of Physics. [DOI: 10.1063/1.1625106]

Ferroelectric materials are very attractive for various technological applications in integrated miniature devices such as memories, sensors and actuators, infrared imaging, optical displays, etc.1 There is increasing interest in investigations on the effect of size reduction on the properties of ferroelectrics.2,3 For ultrahigh density integration of ferroelectric structures into silicon-based microelectronics technology, it is critical to understand the scaling behavior of individual nanosized ferroelectric cells grown on single crystalline substrates.

Various techniques have been utilized to prepare ferroelectric nanostructures on substrates, such as focused ion-beam milling,4 electron-beam direct writing,5 or nanoimprint lithography.6 In the present work, a nanofabrication technique called natural lithography7 or nanosphere lithography,8 which was previously used to fabricate metal nanostructures, is utilized here to prepare oxide ferroelectric nanostructures on substrates. Simply, the essence of this technique is to use well-ordered close-packed latex sphere monolayers as deposition masks. Pulsed laser deposition (PLD)9 is chosen to deposit ferroelectric oxide materials into the triangular interstices to form well-ordered arrays of nanostructures. This way, periodic arrays of pyramid-shaped ferroelectric nanostructures with well-defined lateral dimensions can be obtained.

The grain-size effect on structure and properties of barium titanate has attracted strong interest for several decades.10–13 It is generally observed that with the decrease of grain size, the cubic-to-tetragonal phase transition shifts down towards room temperature due to the increase of internal stress. It is believed that there is a critical grain size, below which the lattice changes from tetragonal to cubic and ferroelectricity is lost. Based on crystal structure studies in ultrafine particles, Uchino et al.12 estimated a critical size of about 0.1 μm for BaTiO$_3$. However, recent structural studies on polycrystalline ceramics by Frey and Payne13 indicate the retention of a long-range cooperative driving force at a grain-size well below 0.1 μm. These previous studies were focused on polycrystalline ceramics or powders. Clearly, detailed studies on the size reduction effect for BaTiO$_3$ are still needed, especially for the case of isolated nanostructures integrated on semiconductor substrates which may exhibit different boundary conditions from those in bulk ceramics or powders. In this letter, we report the retention of ferroelectricity in pyramid-shaped barium titanate nanostructures arranged in a well-ordered manner on a single crystalline substrate.

The latex sphere monolayer deposition mask was prepared on a conductive (100) Nb-doped SrTiO$_3$ single crystalline substrate (0.5 wt % of Nb) by a spin-coating process. Commercial monodisperse polystyrene latex spheres of 1 μm in size were used. Figure 1 is a scanning electron microscopy image of the monolayer. The bright regions in the image correspond to stacking faults in the monolayer. The monolayer-on-substrate was then transferred into a pulsed laser deposition system with a background pressure of 1 × 10$^{-8}$ Torr. A stoichiometric BaTiO$_3$ ceramic target was used. The deposition was carried out at room temperature...
using a KrF excimer laser with an energy of 400 mJ and a repetition rate of 1 Hz. Pure oxygen was used as the background gas and the typical chamber pressure during deposition was $1 \times 10^{-6}$ Torr. The typical deposition time was 10 min. After deposition the polystyrene latex spheres were lifted off in methylene chloride and the as-deposited nanostructures were then annealed in air. The typical annealing conditions were 650 °C for 1 h.

The topography of the annealed nanostructures was examined using a commercial Dimension 5000 atomic force microscope (AFM) from Digital Instruments. Figure 2 presents tapping-mode AFM images of the barium titanate nanostructures obtained using a standard silicon tip with a radius less than 10 nm. Figure 2(a) is a top view, showing that well-ordered arrays of nanostructures were formed, which exhibit a hexagonal arrangement. The individual nanostructures have a triangular shape. At the boundary of the well-ordered region there are some larger structures which are attributed to stacking faults present in the latex sphere monolayer, cf. Fig. 1. Figure 2(b) is a surface plot showing a three-dimensional view of a $4 \mu \text{m} \times 4 \mu \text{m}$ well-ordered area. A surface profile of the nanostructures is displayed in Fig. 2(c). It can be shown that the nanostructures have a pyramid-like shape, i.e., three side facets converge into the vertex point. Typically, an individual pyramid has a height of around 45 nm and a width around 200 nm at half its height.

Nanoscale piezoresponse studies were carried out using scanning force microscopy to investigate whether the nanopyramids shown in Fig. 2 retain ferroelectricity. The experimental setup consists of a commercial scanning probe microscope (SPM) system from ThermoMicroscopes, an ac voltage source, a lock-in amplifier, and a dc voltage supply. A commercial silicon cantilever with a typical force constant $k = 40 \text{ N/m}$ with conductive coating (TiN) was used, which has a typical tip radius less than 35 nm. For piezoresponse measurements the SPM was set to operate in contact mode at a constant force. Both piezoresponse domain images and hysteresis loops were recorded. For piezoresponse imaging, a small ac voltage with a frequency of 16.52 kHz was applied between the tip and the conductive Nb-doped SrTiO$_3$ substrate, and the induced small mechanical oscillations were detected using a lock-in amplifier. The hysteresis measurements were performed using a continuous dc bias source connected in series with the ac voltage source and the loops were obtained by sweeping the bias voltage and recording the piezoresponse signal.

Figure 3 presents a simultaneously obtained topographical image [Fig. 3(a)] and piezoresponse domain image [Fig. 3(b)] of an annealed barium titanate nanoparticle array. The piezoresponse measurements show that most of the annealed, unpoled nanopyramids have the spontaneous polarization downward (dark contrast). Figure 4 is a typical piezoresponse...
response hysteresis loop obtained in a dark region. Piezoresponse hysteresis loops with similar shape were also obtained on those nanopyramids (upward polarization) with bright domain contrast indistinguishable from the background as shown in Fig. 3. Despite the noise level, the piezoresponse hysteresis loop shows clearly that the obtained BaTiO$_3$ nanopyramid arrays (45 nm height, 200 nm width at half their height) are still switchable and ferroelectricity is retained. As can be seen in Fig. 4, there is a negative offset in the piezoresponse hysteresis loop. Similar offsets were observed in piezoresponse measurements for lead zirconate titanate mesoscopic structures prepared on SrTiO$_3$:Nb conductive substrates,$^{15}$ which was suggested to be caused by the possible domain pinning at the ferroelectric-bottom electrode interface. Considering the noise level, the measured piezoresponse $d_{33}$ in the nanosized BaTiO$_3$ is relatively small. Apart from the intrinsic size scaling effect, the apparent decrease of piezoresponse in ferroelectric nanostructures can partly be caused by some other factors such as the crystalline quality of the nanostructures and the suppression of piezoresponse by SPM tips. Further studies are necessary to clarify this issue.

In summary, well-ordered periodic BaTiO$_3$ arrays of nanopyramids were prepared by PLD using a deposition mask consisting of a latex sphere monolayer. Piezoresponse characterization was carried out on the annealed nanostructures, and retention of ferroelectricity in the barium titanate nanopyramids has been proven by piezoresponse hysteresis loops.

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