Epitaxial BiFeO$_3$ nanostructures fabricated by differential etching of BiFeO$_3$ films

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We report on differential etching behavior of the different orientations of the polarization in BiFeO$_3$ (BFO), similar to other ferroelectrics, such as LiNbO$_3$. We show how this effect can be used to fabricate epitaxial BiFeO$_3$ nanostructures. By means of piezoresponse force microscopy (PFM) domains of arbitrary shape and size can be poled in an epitaxial BiFeO$_3$ film, which are then reproduced in the film morphology by differential etching. Structures with a lateral size smaller than 200 nm were fabricated and very good retention properties as well as a highly increased piezoelectric response were detected by PFM. © 2011 American Institute of Physics. [doi:10.1063/1.3630027]

One of the most promising multiferroic materials with respect to applications is BiFeO$_3$ (BFO), being one of the few multiferroics showing ferroelectric and antiferromagnetic order at room temperature. BFO is ferroelectric with a high spontaneous polarization of $\approx$100 $\mu$C/cm$^2$ along the pseudocubic [111] direction, accompanied with a slight distortion from cubic to rhombohedral. BFO has a G-type antiferromagnetic order perpendicular to the direction of ferroelectric polarization and it has been shown that a ferroelectric/ferroelastic switching results in a reorientation of the antiferromagnetic plane as well.

In relation to potential utilization of BFO in data storage technologies, as well as for fundamental investigations, BFO nanostructures have to be fabricated and the influence of size effects on the functional properties studied. In particular, the polarization switching behavior and ferroelectric/ferroelastic domain formation within BFO nanostructures are of interest. Previously reported studies about patterning of BFO applied focused ion beam (FIB) milling to obtain nanostructures from an epitaxial film. The main drawback of FIB milling is the high density of defects and Ga-implantation in the microstructures as well.

In this paper, we report on differential etching behavior of epitaxial and non-polar domains. The fabrication of BFO nanostructures by FIB is, therefore, limited.

In this paper, we report on differential etching of epitaxial (001)-oriented BFO films and how this property can be used to achieve BFO nanostructures in a simple way, with less defects compared to FIB machined ones. Differential etching refers to a different etching rate of different ferroelectric polarization orientations and is already known for a long time in case of other ferroelectric materials, such as BaTiO$_3$, YMnO$_3$, and LiNbO$_3$. The main application of differential etching has been the visualization of the ferro-

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As depicted in Fig. 2(a), epitaxial (001)-oriented BFO films can have eight different ferroelectric domains, four domains where the polarization is directed upwards ($P^+ = P_1^+, P_2^+, P_3^+, \text{and } P_4^+$) and four domains where the polarization is directed downwards ($P^- = P_1^-, P_2^-, P_3^- \text{, and } P_4^-$). We observed that on (001)-oriented BFO films, the four domains pointing upwards ($P^+$) exhibit a much higher etching rate than the domains pointing downwards ($P^-$) when treated with diluted HF. Figures 2(b)–2(d) show the topography, vertical PFM (VPFM), and lateral PFM (LPFM) images of the BFO film, respectively, before etching. In the VPFM images a bright/dark contrast corresponds to polarization pointing downwards/upwards, an intermediate color corresponds to a reduced piezoresponse. In case of LPFM images, a bright/dark contrast corresponds to a polarization pointing to the right/left side of the image. By applying a DC voltage of ±8 V to the tip during scanning, an area of $600 \times 600 \text{ nm}^2$ of the BFO film was switched to domains pointing downwards, $P^-$, surrounded by domains pointing upwards, $P^+$. Figures 2(e)–2(h) show topography, its corresponding scanline, VPFM and LPFM of the same area after etching in the HF solution, respectively. By comparing Figs. 2(c) and 2(f), it can be seen that the domains $P^+$, the negative end of the dipole, remain almost unetched, whereas the domains $P^-$, the positive end of the dipole, are etched orders of magnitude faster. This high differential etching ratio is similar to LiNbO$_3$ and allows the utilization of this effect for structure fabrication. However, in case of LiNbO$_3$, the negative side of the dipole and, therefore, the opposite side compared to BiFeO$_3$ is etched, although BiFeO$_3$ and LiNbO$_3$ have the same crystal symmetry and very similar ion displacements. Therefore, the different cations, which lead to a different surface chemistry, seem to be a crucial factor.

As can be seen in Fig. 2(g), the complete film is switched to domains $P^-$ after the etching procedure, which terminates the fast etching rate. The lateral domains in the structure remain unchanged, whereas the lateral domains in the etched region switch partly together with the out-of-plane direction. Presumably, the switching from $P^+$ to $P^-$ is a result of the instability of domains $P^+$ when the BFO film becomes very thin and is still in contact with HF. In very thin BFO films (e.g., 50 nm), $P^+$ domains written by PFM switch back directly to $P^-$ under the influence of HF, which is the predominant domain state in the as-grown film as well. Hence, the fabrication of nanostructures in our very thin films by this method has not been possible. It has already been shown that the direction of polarization in ferroelectrics can be influenced by the chemical environment. In particular, the out-of-plane polarization in BFO films can be switched by oxygen plasma. A chemical switching of our thin BFO films under the influence of HF is, therefore, reasonable.

To verify the ferroelectric nature of the nanostructures, piezoelectric hysteresis loops on top of the structures were measured. The smallest structures were achieved by poling an area of $200 \times 200 \text{ nm}^2$ in the as-grown film. Figure 3(a) shows the topography of such a domain after subsequent etching in the HF solution and Fig. 3(b) the corresponding scanline across the structure. The full width at half maximum is about 170 nm and using this value the aspect ratio is approximately $a \approx 0.7$. Remanent hysteresis loops were measured by applying a stepwise DC voltage to the bottom electrode and measuring the PFM response in between the voltage steps at zero DC voltage. Figure 3(e) shows a comparison of the remanent hysteresis measured on the nanostructure shown in Figure 3(a) and measured on the same film at an area of the film unexposed to the acid. The piezoelectric response on the structure is highly enhanced compared to the film, which is likely due to the removal of the substrate clamping effect. An increased piezoelectric response was already reported on Pb(Zr,Ti)O$_3$ nanostructures.
and attributed to two effects: on one hand to the removal of the clamping effect and on the other hand to the enhanced mobility of the $90^\circ/C14$ domain walls in the nanostructures.\cite{18,19}

Poling of the BFO structure is possible and good retention properties were observed. Figures 3(c) and 3(d) show the VPFM images before and after the hysteresis measurements, leaving the structure in the switched state. After one week, no retention loss could be detected.

In conclusion, BiFeO$_3$ exhibits differential etching rates for the different out-of-plane orientations of the polarization, similar to other ferroelectric materials, like LiNbO$_3$. When exposed to HF, the positive end of the dipole is etched, whereas the negative end of the dipole remains mainly unetched. We demonstrate the possibility to use this effect for fabrication of nanostructures down to 170 nm in lateral size. The nanostructures retain their ferroelectricity and show very good retention properties. The out-of-plane piezoelectric response on the 170 nm structure is highly enhanced compared to the unpatterned film. By further optimizing the etching parameters, like the etching time and acid composition, it may be possible to achieve smaller nanostructures. This is a promising route for fabrication of epitaxial BiFeO$_3$ nanostructures and study their size effects.

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\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(Color online) Topography (a) and its corresponding scanline (b) of a BiFeO$_3$ nanostructure. VPFM image before (c) and after (d) hysteresis measurement, leaving the structure in the switched state. Scale bar in (a) is 200 nm. (e) PFM hysteresis measured on top of the structure and on the film.}
\end{figure}