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Investigation of AFM-based machining of ferroelectric thin films at the nanoscale

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Abstract

Atomic force microscopy (AFM) has been utilised for nanomechanical machining of various materials including polymers, metals, and semiconductors. Despite being important candidate materials for a wide range of applications including data storage and actuators, ferroelectric materials have rarely been machined via AFM. AFM-based machining of ferroelectric nanostructures offers advantages over established techniques, such as bottom-up approaches and focussed ion beam milling, in select cases where low damage and low-cost modification of already-fabricated thin films are required. Through a systematic investigation of a broad range of AFM parameters, we demonstrate that AFM-based machining provides a low-cost option to rapidly modify local regions of the film, as well as fabricate a range of different nanostructures, including a nanocapacitor array with individually addressable ferroelectric elements.

1. Introduction

Physical modification of materials at the nanoscale in functional materials is essential for numerous nanotechnology-based applications as well as fundamental investigations into their functional behaviour.¹ One of the approaches to achieve this end is atomic force microscopy (AFM)-based machining, where a force is applied via a sufficiently stiff AFM probe to mechanically remove material locally from the sample.^{2–4} Also referred to as mechanical scanning probe lithography or nanomechanical machining, this technique has been utilised in a number of recent studies to, e.g., fabricate complex arrays of 3D nanodots on polymer polycarbonate samples⁵ and nanochannels of varying depth in silicon,⁶ reproduce photographs on a polished aluminium disk,⁷ and form single photon emitters via nanoindentations on a polymer film.⁸ The analysis of AFM-based machining behaviour has been utilised to characterise the hardness of materials in nanoscale sclerometry measurements,⁹ and AFM-based machining has also been used to precisely remove material from regions of the sample surface in

tomography investigations.^{10–13} Given the simplicity of this approach, one would expect that it could be adapted to ferroic materials, which find extensive applications in data-storage, and in particular to ferroelectric oxides where there is strong interest in both the fabrication of nanostructures¹⁴ and volumetric investigations.^{15–17} Despite this promising utility, few AFM-based machining studies have been applied to ferroelectrics^{18–20} (i.e., materials possessing a spontaneous polarisation that is reversible under an applied electric field). One notable exception is the recent work by Steffes et al.,¹⁸ where volumetric imaging of ferroelectric domains in a BiFeO₃ thin film was achieved through sequential nanometric removal of layers of the film with a large ($\sim 11.4 \mu\text{N}$) loading force while monitoring the domain structure via piezoresponse force microscopy (PFM).

The electric-field switchable polarisation of ferroelectrics along with large piezoelectric response, nanoscale conductive anomalies, and above bandgap photovoltaic behaviour enable a range of potential applications relevant to data storage, nanoelectronics, and sensors.^{21,22} With the continuing miniaturisation of electronic devices, numerous studies have

focussed on fabrication of ferroelectric nanostructures so as to minimise the size of the switchable ferroelectric elements.²³ The effect of mechanical boundary conditions such as epitaxial strain, substrate clamping, and localised stress have been shown to have a pronounced effect on the properties of a number of ferroelectric materials.^{24–27} As such, studies have also involved fabrication of ferroelectric nanostructures as a means to alter the mechanical boundary conditions imposed on the ferroelectric material and provide further physical insight into different ferroelectric phenomena mediated through the release of mechanical constraints.^{26,28,29} Such nanostructures have conventionally been fabricated through a range of bottom-up (mask-assisted pulsed laser deposition,³⁰ block co-polymer self-assembly³¹) and top-down (focussed ion beam (FIB),³² electron beam writing³³ and AFM-assisted crystallisation³⁴) techniques. In ferroelectric samples, tomography investigations have typically been achieved by carefully polishing relaxor ferroelectric ceramic samples,³⁵ repeated surface chemical etching of bulk $\text{Pb}(\text{Zr,Ti})\text{O}_3$,³⁶ or via non-destructive confocal Raman microscopy of both periodically poled as well as more complex dendritic electrically-induced domains in LiNbO_3 .^{37,38} In this context, AFM-based machining provides an alternative low-cost option to both fabricate nanostructures as well as undertake tomographic functional investigations, while avoiding problems related to ion-injection from FIB,³⁹ mask limitations (where the nanostructure is limited by the shape and dimensions of the mask) with mask-assisted bottom-up approaches¹⁴ and low resolution ($\sim 1\text{ }\mu\text{m}$) of confocal Raman microscopy.¹⁸ The AFM setup also enables data to be collected in-situ during the machining process, thereby providing insight into the mechanical as well as functional properties, such as the conductivity, of the material.¹⁸ In order to exploit these advantages, the technique must be able to reliably machine a broad range of depths into the ferroelectric sample and also be able to fabricate reproducible nanostructures with small ($< 100\text{ nm}$) lateral dimensions for high-density applications. The sensitivity and precision of AFM enables a range of parameters such as loading force, tip velocity, scan angle, etc. to be varied; all of which can be used to control the machining process, as has been observed on a range of different materials.^{40–42} However, the effect of these parameters on a ferroelectric thin film is largely unknown. In particular, the effect of loading forces exceeding $20\text{ }\mu\text{N}$, where larger depths (10s of nm) of material can be removed in a single pass of the AFM tip, has not been investigated. In examining the effect of these parameters, the capability and limitations of the technique to fabricate ferroelectric nanostructures needs to be explored.

In this work, we systematically investigate the effect of AFM parameters on the machining behaviour of an epitaxially-

strained thin film of BiFeO_3 , a lead-free ferroelectric where the epitaxial constraint gives rise to a coexistence of different phases. Such films are prime candidates for magnetoelectric, piezoelectric, and nanoelectronic devices.^{43–45} Here, the conditions required to thin local regions of such a mixed phase BiFeO_3 film to a range of depths are theoretically predicted and experimentally demonstrated, which could be utilised for fabrication of complex 3D nanostructures, measurement of certain properties as a function of thickness, or in some cases alteration of ferroelectric properties due to local changes in film thickness.^{18,46} A framework is established to determine the optimum conditions required to fabricate nanostructures with the smallest lateral dimensions possible in the film. Finally, the possibility for fabricating a range of different nanostructures is explored.

2. Materials and Methods

In this work, $\sim 50\text{ nm}$ thick epitaxial $\text{BiFeO}_3/\text{Ca}_{0.67}\text{Ce}_{0.33}\text{MnO}_3/\text{LaAlO}_3$ and $\text{BiFeO}_3/\text{LaSrMnO}_3/\text{LaAlO}_3$ films were used. Both films were fabricated by pulsed laser deposition with a KrF excimer laser ($\lambda = 248\text{ nm}$). The laser fluence and repetition rate were fixed at 0.63 Jcm^2 and 8 Hz respectively. The target and substrate distance were set at 5.5 cm , while the films were deposited in an ambient oxygen pressure of 15 Pa and a deposition temperature of $680 - 700\text{ }^\circ\text{C}$. Cr-Au electrodes $\sim 70\text{ }\mu\text{m}$ in diameter comprising 5 nm of Cr and 2 nm of Au were evaporated onto the BiFeO_3 films through a shadow mask using an electron beam evaporator (DE400, DE Technology, USA) at a rate of $0.4\text{ }\text{\AA}/\text{s}$ in vacuum.

Diamond AFM probes (NM-RC and NM-TC, Adama Innovations Ltd., Ireland) with a spring constant, k , of 130.57 N/m and 117.07 N/m , respectively (as calibrated via the Sader method),⁴⁷ were used in contact mode for all machining operations. It should be noted that the spring constant calibration can have an uncertainty of up to $\pm 10\%$.⁴⁸ The deflection sensitivity of both cantilevers was determined by carrying out a 10×10 array of force distance curves post machining on a thick diamond film, providing values of $46.6 \pm 0.1\text{ nm/V}$ for the NM-TC tip and $44.1 \pm 0.1\text{ nm/V}$ for the NM-RC tip. To extract mechanical properties and fabricate nanostructures, the NM-RC probes were used, which have a nominal tip radius of $10 \pm 5\text{ nm}$. NM-TC probes were used for the thinning experiments and have a larger nominal radius of $25 \pm 10\text{ nm}$. Both probe types have a $\sim 90^\circ$ opening angle. Residual pile-up of material due to machining operations was subsequently removed by imaging of the region with a small, non-destructive loading force ($\sim 1\text{ }\mu\text{N}$) using the same diamond probe (demonstrated in supplementary Figure S1). Before and after each machining experiment, the

profiles of the diamond probes were evaluated by blind tip reconstruction, after scanning a tip characterisation grating (TGT101, MikroMasch, Germany), as shown in supplementary Figure S2.^{49,50} Although the diamond probes are also capable of imaging the resulting machined features (see supplementary Figure S1), sharp Si probes (PPP-NCHR, Nanosensors, Switzerland) were used to obtain all of the topography images shown in this work to minimise any artefacts due to machined residue on the tip or the oblique opening angle of the diamond probes. Conductive PtIr₅ coated Si probes (PPP-EFM, Nanosensors, Switzerland) were used to acquire piezoresponse and conductivity images. All experiments were carried out using

a commercial AFM (Cypher, Asylum Research, USA). It should be noted that the inclination angle between the cantilever and sample is $\sim 11^\circ$, while the sample typically had a tilt of $\sim 1^\circ - 2^\circ$ with respect to the cantilever, as determined from unflattened images. Vertical PFM (VPFM) images and local hysteresis loops were obtained using the built-in Dual AC Resonance Tracking (DART) mode, with a 1 V_{AC} imaging bias, centred around a contact resonance frequency of ~ 330 kHz.⁵¹

3. Results and Discussion

3.1 AFM-Based Machining for Material Thinning

Fig. 1. Effect of different AFM parameters on the thinning of local regions of a mixed phase BiFeO₃ film. (a) Topography after applying a matrix of loading forces and separations between adjacent scan lines at a constant velocity of 0.25 $\mu\text{m/s}$. (b) Topography after applying a matrix of loading forces and tip velocities at a constant line-separation of 10 nm. Variation in machined (c) depth and (e) roughness (rms) from (a). The dashed lines with hollow symbols labelled “est” describe the corresponding depths estimated by the nanochannel depth prediction model.⁵² Variation in machined (d) depth and (f) roughness (rms) from (b). Values in (e, f) where machining has occurred can be seen to have a larger roughness than the 0.8 ± 0.2 nm (rms) of the as-grown film, which is represented by the grey shaded region. The applied force values have an uncertainty of $\pm 10\%$.⁴⁸

A key aspect of AFM-based machining involves material removal to thin local regions of the sample. As mentioned previously, this would have direct implications towards the

fabrication of 3D nanostructures, tomography related applications, and/or probing novel ferroelectric phenomena. For optimal thinning to be realised, the ability to reliably predict

depths and achieve desired smoothness of the machined surface is required. Here, 500×500 nm regions are machined by scanning the NM-TC tip from top to bottom with a large loading force over a number of closely spaced (10, 30, and 60 nm) adjacent lines. The machining was carried out via single pass lines (i.e., lines were drawn manually in lithography mode so no retrace was carried out) to compare the results to the nanochannel depth prediction model described in Geng et al.⁵² The removal depth and resulting roughness (root mean squared (rms)) were examined as a function of varying applied loading force, separation between adjacent machined lines, and tip velocity.

Figure 1(a) shows the AFM topography image of a region of the film after application of varying loading forces using three different separations between adjacent lines. This was carried out at a constant velocity of $0.25 \mu\text{m/s}$, which was selected based on preliminary testing. The mixed phase BiFeO_3 film consists of a coexistence of rhombohedral-like R phase, which comprises the banded needle-like structures within a tetragonal-like T phase matrix. Due to a combination of the tip size and a possible softening of material adjacent to the machined regions (which is then removed during machining of subsequent lines), the resulting machined boxes have rectangular dimensions of approximately 1000×500 nm. At a glance, it can be seen that the largest line-separations and lowest loading forces result in no material removal. The depth increases with loading force and decreases with line-separation. The average depth and roughness of each machined box (analysed over a constant area per box) is shown quantitatively in Figure 1(c) and 1(e), respectively. The depth was obtained by first aligning (via MATLAB) the topography images before and after machining, such that the difference in height on the unmachined regions of the before and after images was minimised. The average height of an array of 25×25 pixels within the machined squares was then subtracted from the average height of an array of pixels over the same region before it was machined so as to account for the initial variations in height due to the mixed phase topography. The scans before and after machining were taken with the same pixel density (512×512 pixels over $100 \mu\text{m}^2$), in turn enabling the sample area over which the change in depth is measured to be the same. The depth and standard deviation values are plotted in Figures 1(c) and 1(d). For the largest line-separation of 60 nm, which is slightly larger than the measured NM-TC tip radius of ~ 40 nm (see supplementary Figure S2), machining does not occur until $82 \mu\text{N}$ is applied. In contrast, for the lowest line-separation of 10 nm, machining occurs for loading forces $\geq 49 \mu\text{N}$. The machined depth at $99 \mu\text{N}$ load also increases dramatically from 17 ± 2 nm for 60 nm line-separation, to 45 ± 6 nm for 10 nm line-separation, highlighting the strong effect of

varying line-separation with the increased overlap between adjacent machined lines at low separations effectively enabling repeated machining over the same regions and an increased depth.^{6,49} The shallowest machined depth of 0.9 ± 0.3 nm was obtained with $49 \mu\text{N}$ load at a 10 nm line-separation. This is similar to the gradual (< 1 nm) removal of material observed in a number of previous works.^{10,13,18} In the aforementioned studies, such gradual removal was initiated, in some cases, after repeated scanning with a relatively smaller ($\sim 11 \mu\text{N}$) loading force. Hence, it is feasible that repeated scanning with the parameters where no machining was observed may lead to comparable behaviour, i.e., removal of material in a manner similar to that associated with the ploughing regime, where plastic deformation begins to occur.^{41,53} As expected, the larger forces used here enabled a more rapid removal of material.

Additionally, a 3×6 grid of 500×500 nm regions were machined at a constant line-separation of 10 nm, while varying the tip velocity and applied loading force. The topography of these machined regions is shown in Figure 1(b), while the measured depth and roughness are shown in Figures 1(d) and 1(f), respectively. Little variation in the depth or roughness is observed with different tip velocities, aside from at the larger loading forces ($\geq 58 \mu\text{N}$) where a slight increase in depth is observed at the two slower tip velocities within the errors. At the largest force and slowest tip velocity, the depth obtained was 56 ± 3 nm, exceeding the film thickness and resulting in partial removal of the bottom electrode. When machining to depths approaching the film thickness, it is difficult to determine whether or not the bottom electrode has been partially machined; however, assuming the bottom electrode has a similar or lower yield stress compared to the BiFeO_3 film (as both materials are perovskite films), it is likely that some of the bottom electrode was removed as well. Some deviation in depth between the squares machined by identical parameters in the machining experiment is evident, as shown in Figures 1(c) and 1(d). More specifically, physical removal of material begins at a lower loading force in the experiment using a varying velocity, in comparison to the experiment using a constant velocity. This deviation highlights additional uncertainty at low loading forces that could occur due to variations in tip contact area across the surface, mechanically-induced phase transformations,⁴⁵ machined pile-up at the tip apex, and a reduction in the tip-sample friction, which is known to occur at low machining depths.⁴¹ Meanwhile, the machined depths at larger loading forces are more consistent between experiments. Such behaviour is analogous to FIB milling, where additional considerations are required in some cases when milling to nanoscale depths, as opposed to microscale depths.^{54,55}

In analysing the roughness more closely – as a function of line-separation and loading force in Figure 1(e), and tip velocity and force in Figure 1(f) – the clearest trend is the increase in roughness with depth. For instance, at the lowest machined depths (0.9 ± 0.3 nm), the measured roughness (0.8 nm) is similar to the average roughness measured across various 500×500 nm regions of the as-grown sample (0.8 ± 0.2 nm), as indicated by the baseline in Figures 1(e) and 1(f). While at increased depths, the roughness reaches much higher values of 3 – 8 nm. The dispersion in roughness values despite identical machining parameters being used in some cases (e.g., 66 μ N at 0.25 μ m/s and 10 nm line-separation in Figures 1(e) and 1(f)), further highlights the aforementioned deviation in machining behaviour, which could also be related to factors such as redeposition of machined residue. Although the roughness values at varying separations appear similar, the increased depth at 10 nm line spacing alludes to that particular separation enabling the deepest and smoothest machining. Additionally, it may be possible to machine with large depths via application of larger loading forces and reduce the roughness via subsequent scans with lower ($\sim 40 - 60$ μ N) forces in a ‘cut and polish’ type of approach. Meanwhile, no clear variation in roughness is observed with varying tip velocities as has been observed in AFM-based machining studies on other materials.⁵⁶

Experimental data was compared to predictions made from the model used in Geng et al.⁵² This model was chosen as it accounts for line-separation, and does not require precise values of the Young’s modulus, which is known to exhibit substantial variation in mixed phase BiFeO₃, both spatially across the film (between the R and T phases) and with a range of different values quoted in literature.^{57–59} The model approximates the machining process as a hard abrasive particle sliding over a softer sample. The loading force (F_N) is given as the product of the yield stress, σ_y , multiplied by the horizontally projected area of interface A_T .

$$F_N = \sigma_y A_T \quad (1)$$

A_T is dependent on the line-separation Δ , as well as the effective tip radius R' at the machined depth h . As shown in supplementary Figure S2(f), the tip used here can be approximated by a truncated cone with a tip half angle (α_{tha}) of $54 \pm 1^\circ$ with a flat circular apex with radius of 39.5 ± 0.5 nm. Hence, A_T can be approximated as follows.⁵²

$$A_T = \frac{1}{3} (2R' - \Delta) \sqrt{(2R' - \Delta)\Delta} + \frac{1}{2} \arccos \frac{R' - \Delta}{R'} R'^2 - \frac{1}{2} (R' - \Delta) \sqrt{R'^2 - (R' - \Delta)^2} \quad (2)$$

where R' is described in terms of h , the tip radius R_0 and α_{tha}

$$R' = (h - R_0(1 - \sin \alpha_{tha})) \tan \alpha_{tha} + R_0 \cos \alpha_{tha} \quad (3)$$

Using the value for σ_y of 71.1 ± 15.9 GPa, as estimated from AFM nanoindentation experiments (supplementary information, Figure S3), the predicted machined depth h can be determined using the above equation. These are shown as dashed lines in Figures 1(c) and 1(d). The large uncertainties propagate from the uncertainty in σ_y . The estimated depths tend to compare well at larger loading forces but deviate at lower loading forces. This may be due to the model not accounting for factors such as elastic recovery, friction, surface roughness, and the influence of the machined pile-up material. Such observations are similar to those previously obtained on metals,⁵² where larger machined depths (> 50 nm) were predicted more accurately than smaller ones.

The ability to control the machined depth in thin films enables the study of the variation in properties as a function of depth, as well as fabricating 3D nanostructures. As a basic example, of the former, a conductive AFM (cAFM) scan (supplementary information, Figure S4) demonstrates that current increases for machined depths ≥ 50 nm, indicating that the tip has machined through the insulating ferroelectric film to the conductive bottom electrode below. Such observations can provide an indication of film thickness, with an average estimated thickness of 48 ± 1 nm.

3.2 AFM-Based Machining for Nanostructure Fabrication

In exploring the potential of AFM-based machining for nanostructure fabrication, a crucial aspect involves determination of the sharpest possible feature (i.e., maximum depth and minimum width) that can be reliably fabricated with the AFM tip. Nominally, this would depend on parameters related to the profile of the tip (such as the half angle and tip radius) as well as the film thickness. For instance, the BiFeO₃ film is ~ 50 nm thick, while the reconstructed profile of the NM-RC tip (used for the remaining experiments in this work) can be modelled by a rounded cone with a radius of 2.5 nm and a half angle of 43° . From this, the diameter of the tip at 50 nm from the apex is ~ 105 nm in diameter, and so could ideally enable features to be machined through the thickness of the film that are slightly greater than ~ 105 nm in width, or features that have a depth of 5 nm and width of ~ 25 nm, with the tip being effectively utilised as a nanoscale diamond scribe. To determine if these depth versus width relationships hold true, we investigated the effect of different AFM parameters on the machined depth and width of single lines.⁶⁰

Fig. 2. The effect of machining angle. (a) Topography of a $12 \times 12 \mu\text{m}$ region of the BiFeO_3 film after machining four circles that are $2.5 \mu\text{m}$ in diameter using a loading force of $70 \mu\text{N}$ at $0.5 \mu\text{m/s}$. The sample was rotated to 0° (top left), 32° (top right), 62° (bottom left), and 90° (bottom right) for the four circles, so as to isolate machining angle-related effects. The inset image in (a) shows the cantilever (white arrow) angle with respect to the sample (grey background) which corresponds to each circle. The red arrows show the machining direction and position where the machining angle is 0° . α_m is defined as the angle between the long axis of the cantilever and the tip motion direction as schematised in supplementary Figure S5. (b) The machined depth, machined α_{ha} (half angle of the machined line), and the lateral deflection of tip versus α_m for different sample rotation angles.

The effect of machining angle α_m (i.e., the direction of the tip relative to the sample) on machined depth and width was examined by machining a series of circles encompassing the effect of all possible angles. To exclude external effects such as the crystallisation direction of the film and the tip-sample azimuthal angle, the sample was physically rotated anticlockwise to 4 different angles (0° , 32° , 62° , and 90°). Figure 2(a) shows the topography after machining the circles at these four rotated angles at a constant force of $70 \mu\text{N}$ with $0.5 \mu\text{m/s}$ tip velocity. These force and tip velocity values were chosen based on preliminary measurements resulting in significant machined depths without exceeding the thickness of the thin film. The red arrow in each circle represents the tip location and machining direction at 0° (i.e., when the machining angle is parallel to the long axis of the cantilever). The value of the machined depth and half angle of the machined line, α_{ha} (indicative of width and sharpness), at each α_m was then determined by cross-section analysis across the machined lines (schematised in supplementary Figure S5). Each of the four machined circles show similar variations in machined depth and α_{ha} with α_m , as shown in Figure 2(b), thereby excluding non-machining angle-related effects.

Another advantage of using AFM in these studies is that data can be acquired in-situ during machining. The lateral deflection signal, proportional to the force across the short axis of the

cantilever, is shown in Figure 2(b) (reset to 0 prior to each machining). The machined depth is minimised when α_m corresponds to $\sim 30^\circ$ and $\sim 210^\circ$, at similar values of α_m where the lateral deflection shows local maxima or minima. Although α_{ha} also shows local minima at these α_m , as the machined depth is at a minimum, these angles are a suboptimal choice for achieving the sharpest possible machined features. Meanwhile, α_{ha} shows a strong variation with different machining angles; for instance α_{ha} is smaller for a range of α_m values at $\sim 0^\circ - 50^\circ$ and $\sim 180^\circ - 220^\circ$, when approximately parallel to the cantilever long axis, compared to at $\alpha_m \sim 90^\circ$ and $\sim 270^\circ$, which is perpendicular to the long axis of the cantilever. This variation can be explained by the fact that the calculated spring constant parallel to the cantilever long axis is almost twice that of the spring constant parallel to the short axis (see supplementary information).⁶¹ This observation is also evident in lateral deflections shown in Figure 2(b), as the signal measured when machining roughly parallel to the cantilever long axis is closer to zero compared to other machining angles. An increased lateral deflection and torsion of the cantilever, in turn results in a larger α_{ha} and a wider machined trench due to the geometry of the tip-sample contact. For example, if the tip rotates $\sim 10^\circ$ around the short axis when $\alpha_m \sim 90^\circ$, we can assume the tip would only rotate $\sim 5^\circ$ around the long axis when $\alpha_m \sim 0^\circ$, as it is known (from above) that the cantilever is almost twice as stiff along the latter direction. From studying the reconstructed tip, this

additional $\sim 5^\circ$ tilt would result in a $\sim 15\%$ increase in contact area at a 15 nm depth. The influence of cantilever lateral deflection or torsion on the resulting depth and width has also been suggested in previous AFM-based machining studies on other materials, where the torsion is caused by a combination of friction and the resistance of the material to deformation during the machining process.⁴³ Such an effect could be obviated by

utilising a stiffer cantilever. Although the lateral deflection reaches zero at $\sim 10^\circ - 20^\circ$, this could be due to the increased machined depth which occurs at 0° , in turn resulting in increased torsion. Further study of the machined depth and α_{ha} of straight lines at varying machining angles can be found in supplementary Figure S5. We conclude that a machining angle of 0° can be used to machine the sharpest possible features.

Fig. 3. The effect of varying tip velocity and loading force at a constant machining angle. (a) The topography of a $12 \times 12 \mu\text{m}$ region of the BiFeO_3 film after machining a series of lines that are $1 \mu\text{m}$ in length with varying tip velocity and loading force. (b) Machined depth (with the theoretical estimates denoted by “est”), (c) half angle and (d) width as analysed from (a) as a function of loading force for different tip velocities. The scale bar is $2 \mu\text{m}$.

In order to fabricate nanoscale structures using an AFM tip, it is also essential to study the effect of different loading forces and tip velocities on the depth and width (defined as schematised in supplementary Figure S5(b)) of a single machined line. Figure 3(a) shows a series of straight lines machined with different tip velocities from $0.125 - 2 \mu\text{m/s}$ from left to right, and with different loading forces from $17 - 86 \mu\text{N}$ from top to bottom. All lines were machined at $\alpha_m = 0^\circ$ as it was previously established to give the sharpest machining. At each loading force, the tip velocity was observed to have little effect on the depth of the machined lines, which is similar to what has been observed on other materials⁴⁰. Machining began for tip velocities $< 2 \mu\text{m/s}$ at $17 \mu\text{N}$, and the machined depth increased significantly with the increasing force ($\sim 0.085 \text{ nm}/\mu\text{N}$). The machined depths were also predicted using the nanomechanical model used in Geng et al.⁵² for machining single lines, where

$$A_T = \frac{1}{2} \pi (R_0 \cos \alpha_{tha} + (h - R_0 + R_0 \sin \alpha_{tha}) \tan \alpha_{tha})^2 \quad (4)$$

The NM-RC tip was modelled as a rounded cone with α_{tha} of 47° and R_0 of 2.5 nm , as shown in Figure S2. Repeatability is also evident here, e.g., at a loading force of $\sim 69 \mu\text{N}$ and tip velocity of $0.5 \mu\text{m/s}$ the machined depth ($\sim 24 \text{ nm}$) agrees with the corresponding machined depth in Figure 2. α_{ha} was observed to decrease with increasing loading force. This demonstrates that α_{ha} is larger for the shallowest machined lines, likely due to the larger half angle of the tip itself close to the apex. However, based on the dispersion in the data and the size of the error bars, it is unclear if α_{ha} stabilises or continues to decrease at higher loading forces. The width of the machined lines appears to increase linearly with loading force up until $\sim 43 \mu\text{N}$, after which the rate of increase slows. The width also appears to be affected

by tip velocity. For instance, at larger loading forces, faster tip velocities result in features that are up to ~ 40 nm wider than at slower velocities. It should be noted that when carrying out the experiment, the lines were machined in the order from the slowest to the fastest velocities, and so these results may be influenced by an accumulation of machined material on the tip. Moreover, when carrying out part of the experiment in reverse order, as shown in Figure S6, the variation appears more random, highlighting that velocity likely has a more subtle effect on the machining behaviour. Meanwhile, the relatively large width and α_{ha} of the machined lines compared to the reconstructed profile of the tip could be attributed to the lateral tilt of the tip with the global $11 \pm 2^\circ$ inclination angle between the cantilever and sample, along with additional tilt during machining caused by lateral torsion or buckling of the cantilever. For example, if we account for this global inclination angle along with an additional, say $\sim 10^\circ$ tilt during machining, the contact area estimated from the reconstructed tip at a machined depth of ~ 15 nm increases $\sim 45\%$, compared to a tip without any tilt. An additional factor to the increased machined width could be the effect of mechanically induced phase transformations.

With the effects of different AFM parameters on the depth and width of machined features in this ferroelectric film determined, we proceed to fabricate nanostructures with the smallest lateral features enabled by this method. Here, simple square nanoislands were fabricated by machining two parallel lines at $\alpha_m = 0^\circ$ separated by a defined distance that defines the lateral dimensions of the island. Subsequently, the sample was rotated by 90° and two more parallel lines, separated by the same defined distance were machined at $\alpha_m = 0^\circ$ to create a single nanoisland. From Figure 3, it was observed that a $17 \mu\text{N}$ loading force at $0.125 \mu\text{m/s}$ gave rise to a machined depth just below 5 nm and a width of ~ 70 nm. Using the above parameters, a 90×90 nm nanoisland was machined, as shown in Figure 4(a). The lines were machined longer than 90 nm, so as to accommodate for any microscope drift and guarantee overlap of the orthogonal lines. Line profiles corresponding to the vertical (red) and horizontal (blue) lines in the topography image are shown in Figures 4(a) (ii) and (iii), respectively. The blue horizontal line profile across the first pair of lines machined shows a depth of ~ 5 nm, as expected. However, for the second pair of lines machined (red vertical lines), the machined depth increased to ~ 10 nm despite the observation from Figure 2 that rotating the sample had little effect on the machined depth. This increase in machined depth with the same loading force could be caused by a softening of the surrounding region after the first pair of lines were machined, as has been observed in other materials.⁶² It could also be due to a jolting effect of the tip as it crosses

orthogonally over the previously machined line; this effect is evident when monitoring the lateral deflection of the cantilever (supplementary information, Figure S7), where a decrease in lateral deflection is observed after crossing over the first previously machined line, which coincides with a subsequent increase in machined depth. As evidenced by the line profiles, the top surface of the fabricated island is at the same height as the surrounding surface height, with the black lines highlighting the lateral dimensions of the island.

To increase the machined depth, a $52 \mu\text{N}$ loading force at $0.125 \mu\text{m/s}$ was chosen with an expected depth of ~ 20 nm and width of ~ 100 nm (see Figure 3). Using these parameters, a second nanoisland with 120 nm line-separation was fabricated (supplementary information, Figure S8(a)). Similar to the smaller nanoisland, the line profiles again show that the first pair of lines machined (blue) have a depth of ~ 15 nm whilst the second pair of lines machined (red) are > 25 nm deep. In this case, the width of the machined line does not increase as rapidly between depths of 15 and 25 nm, c.f. 5 and 10 nm; this is likely similar to the effect discussed in Figure 3, where α_{ha} was found to be larger for shallower machined lines.

Fig. 4. Characterization of a 90 nm nanoisland. (a) (i) Topography and line profiles corresponding to the (ii) blue and (iii) red lines. (b) (i) VPFM amplitude and (ii) phase loop on the island. (c) VPFM phase image (i) before and (ii) after acquisition of the hysteresis loop, showing reversal of the measured phase from pointing down to up. (iii) VPFM amplitude after loop acquisition showing a minimum in amplitude around the switched domain corresponding to the induced domain wall.

The ferroelectric properties of these nanoislands were then examined. Figure 4(b) (i) and (ii) show the DART VPFM amplitude and phase hysteresis loops acquired on the 90 nm

island (see supplementary Figure S8(b) for the 120 nm nanoisland). In both cases, full phase reversal is achieved, which is accompanied by a minimum in amplitude, as typically observed for ferroelectrics.⁶³ Compared to loops acquired on the as-grown film (supplementary information, Figure S7), a slight increase in the coercive field at negative bias from the tip (opposite to the initial polarisation direction of the film) is observed. Similar increases in coercive fields have been observed on nanoislands machined by other methods on ferroelectric thin films and have been attributed to defects at the sidewalls of the islands causing increased pinning.⁶⁴ In order to further demonstrate the ferroelectricity of the nanoislands, DART VPFM images before and after loop acquisition are shown from the 90 and 120 nm nanoislands in Figure 4(c) and supplementary Figure S8(c), respectively. In both cases, the initial VPFM phase images (Figure 4(c) (i)) show a uniform polarisation pointing down towards the substrate. As the hysteresis loops were completed following the application of negative bias values, the resulting VPFM phase shows a reversal of polarisation orientation pointing up towards the surface. The switched points were found to be stable over time and are accompanied by a minimum in VPFM amplitude (Figure 4(c) (iii)) at the domain walls. It should be noted that as the machined depth is less than the thickness of the film, switching may not be totally confined to the island as it is still connected to the surrounding film in the region adjacent to the bottom electrode. Nevertheless, the machined trench does appear to limit the propagation of domains from the island to the surrounding film (with one small needle domain propagating to the left of the switched location in the bigger machined island), as evidenced by the shape of the switched domain, which more strongly resembles the shape of the island itself. Another point of interest is that an increase in VPFM amplitude is observed around the periphery of the machined sections. Although possibly caused by topographic cross-talk, such an enhancement has also been observed in PFM studies of other ferroelectric samples that have been subjected to plastic indentation, and has been attributed to the effect of residual tensile strain or increased dislocation activity around the indents.^{65–67}

The dimensions of the nanoislands fabricated in this study highlight the limitations of AFM-based machining in fabricating ultra-high-density nanostructures. For instance, the minimum lateral dimensions of 90 and 120 nm at depths of 5 and 20 nm, are larger than the diameter of the reconstructed tip shown in Figure S2 of ~ 25 and ~ 65 nm at those depths. This difference is likely due to the previously mentioned factors, which result in a widening of the machined lines, including the lateral tilt of the tip during machining. However, despite AFM-based machining comparing unfavourably with bottom-up techniques, which

have previously achieved sub-10 nm islands on ultra-thin (< 2 nm) films,³¹ further improvements could easily be made using stiffer cantilevers, with a higher-aspect ratio tip, on thinner films. Machining on a thinner film would reduce pile-up and more easily enable machining through the thickness of film, in turn resulting in nanostructures that are isolated from the rest of the film. Indeed, a region of the film could potentially be thinned via machining before nanostructure fabrication. A higher-aspect ratio tip would reduce the limitation imposed by the shape of the tip, albeit such a change could come at the cost of lowering the stiffness. While a stiffer cantilever would feasibly result in reduced lateral torsion and deflection, which in turn may enable the widths of the machined features to be closer to the dimensions of the tip itself. This may also reduce the effect of α_m on the machining behaviour, in turn enabling high-density nanostructures to be fabricated without the need to physically rotate the sample, and restricted only by the tip velocities used here (up to $2 \mu\text{m/s}$). Although different tips would give rise to different machining behaviour, the ascribed approach provides a useful tool through which to characterise the machining behaviour and optimise the fabrication of nanostructures. Such a process could be further streamlined via machine-learning approaches.^{68–71}

Fig. 5. Examples of nanostructures that can be fabricated by AFM-based machining. Topography of (a) the University College Dublin harp logo and (b) a 100 nm nanoisland array machined on the BiFeO_3 film. (c) Topography of a machined nanocapacitor array and the corresponding (d) VPFM phase after selectively switching elements with -10 V from the tip into a checkerboard pattern. (e) VPFM phase after applying +10 V to reverse the elements back to their initial state.

Furthermore, AFM-based machining can be readily used to fabricate a range of nanostructures and arrays. For example, more complex patterns can be fabricated, as demonstrated in Figure 5(a) where a harp shape (the University College Dublin logo) has been machined by the tip on the BiFeO_3 film. A

nanoarray consisting of islands 100×100 nm in size, fabricated on the BiFeO_3 film is also shown in Figure 5(b). The array was achieved through the same methods as described for Figure 4, except with longer parallel lines, machined periodically over a larger area. Such arrays could feasibly be fabricated over the entire range of the AFM scanner (e.g., 30 – 100 μm , depending on the microscope used), and scaled-up even further through parallel processing, e.g., millipede-like schemes with arrays of stiff cantilevers.⁷²

In addition to machining the bare surface of a ferroelectric film, AFM-based machining can also be carried out on deposited top-electrodes in order to fabricate a range of electrode structures. Here, a 5 nm film of Cr, followed by 2 nm of Au was evaporated onto a region of a mixed phase BiFeO_3 film. Cr was chosen as an electrode due to its low value of ductility and high brittleness⁷³, enabling pile-up from machining to be easily cleared. While having a top layer of gold is a commonly used technique to improve electrical contact between the tip and film via the electrode. Machining on thicker gold films was also attempted, however, the high ductility of gold led to persistent difficulties in removing the pile-up from machining. The electrode was chosen to be thin (total thickness 7 nm), so as to enable smaller electrode structures to be easily machined.

In order to fabricate a nanoarray on the BiFeO_3 -Cr-Au film, a similar procedure to that described for the bare surface was carried out and shown in supplementary Figure S9. Although in this case only the top electrodes are isolated while the bottom LaSrMnO_3 electrode is shared, similar to the terminology described in previous works where similar structures were fabricated, we describe the resulting nanoarray as a nanocapacitor array.^{74,75} The topography of the fabricated nanocapacitor array is shown in Figure 5(c). It can be seen that the top electrodes on some of the islands have de-laminated, possibly due to poor adhesion. However, most of the nanocapacitor array remained intact. As demonstrated in Figures 5(d) and 5(e), the elements are individually addressable and can be reversibly switched. Through application of negative bias (exceeding the coercive voltage) from the tip to selective elements in a checkerboard pattern, the polarisation switches from pointing down, to pointing up, as indicated by the purple colour in the VPFM phase image in Figure 5(d). With subsequent application of an above-coercive, positive bias from the tip, these elements can then be reversed back to their initial state, as shown in Figure 5(e).

4. Conclusions

The capabilities and limitations of AFM-based machining of ferroelectric thin films has been systematically explored on

epitaxially strained BiFeO_3 . Machining using a broad range of loading forces, separation between adjacent lines, and tip velocities were found to locally thin regions of the film in a single pass to a range of depths by as little as sub-nm and as much as through the thickness of the film into the underlying bottom electrode. Hence, the technique can be used to remove entire layers of material and determine film thickness (in conjunction with cAFM), as well as remove multiple layers of different materials. The results were found to compare favourably to a nanochannel depth prediction model at larger loading forces, with larger deviations at lower forces. A process was also established to obtain nanostructures with the smallest possible lateral dimensions in the film. This involved analysing the effect of different scanning angles, where it was found that scanning parallel to the cantilever long axis gave rise to the sharpest (i.e., deepest and narrowest) features; while examining the effect of different loading velocities and forces revealed that tip velocities had a minimal effect while having a clean tip apex resulted in sharper features at each force and depth. From this, we were able to fabricate individually addressable ferroelectric nanostructures that were at least 5 nm and 20 nm deep, with respective widths of 90 nm and 120 nm. While the lateral dimensions of the islands were larger than the minimum size achievable based on the profile of the tip (~25 and ~65 nm at those depths), further improvements could be achieved with a stiffer, higher-aspect ratio tip. The possibility of fabricating a broad range of nanostructures was also demonstrated and machining could also be achieved on films with Cr-Au electrodes, enabling a proof-of-concept demonstration of a ferroelectric nanocapacitor array.

Supplementary Material

Figures S1 to S9 along with relevant text can be found in the supplementary material.

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Conflict of Interest

J.I.K. is partially funded by Adama Innovations Ltd., manufacturer of the diamond probes used in this study.

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(a) **(b)**

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(a) **(b)** **(c)** **(d)** **(e)**