

**Nucleation, growth, and control of ferroelectric-ferroelastic domains in thin polycrystalline films**Yachin Ivry,<sup>1,\*</sup> James F. Scott,<sup>2</sup> Ekhard K. H. Salje,<sup>3</sup> and Colm Durkan<sup>1,†</sup><sup>1</sup>*Nanoscience Centre, University of Cambridge, 11 JJ Thomson Avenue, Cambridge, CB3 0FF, United Kingdom*<sup>2</sup>*Department of Physics, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom*<sup>3</sup>*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom*

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The unique response of ferroic materials to external excitations facilitates them for diverse technologies, such as nonvolatile memory devices. The primary driving force behind this response is encoded in domain switching. In bulk ferroics, domains switch in a two-step process: nucleation and growth. For ferroelectrics, this can be explained by the Kolmogorov-Avrami-Ishibashi (KAI) model. Nevertheless, it is unclear whether domains remain correlated in finite geometries, as required by the KAI model. Moreover, although ferroelastic domains exist in many ferroelectrics, experimental limitations have hindered the study of their switching mechanisms. This uncertainty limits our understanding of domain switching and controllability, preventing thin-film and polycrystalline ferroelectrics from reaching their full technological potential. Here we used piezoresponse force microscopy to study the switching mechanisms of ferroelectric-ferroelastic domains in thin polycrystalline  $\text{Pb}_{0.7}\text{Zr}_{0.3}\text{TiO}_3$  films at the nanometer scale. We have found that switched biferroic domains can nucleate at multiple sites with a coherence length that may span several grains, and that nucleators merge to form mesoscale domains, in a manner consistent with that expected from the KAI model.

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The behavior of ferroic materials at the nanoscale has garnered much interest in recent years as at this scale “the material is the machine.”<sup>1</sup> These materials are heavily utilized in everyday technologies such as nonvolatile memory devices and medical imaging, signal processing, and radar detectors.<sup>2</sup> Given that the macroscopic properties of ferroics are due to collective phenomena (strain, electric polarization, magnetization), the origins of which are at the nanoscale—the length scale between one and a few domains, studying the domain behavior at this scale can offer useful insights into the different ferroic systems. For instance, ferroelectric<sup>3</sup> and ferroelastic<sup>4,5</sup> domains can be as small as a few nanometers, while ferromagnetic domains are typically much larger due to the difference between the nature of the different domain-wall types.<sup>6</sup>

The essence of ferroic systems is the ability to reversibly switch the characteristic spontaneous strain (electrical, mechanical, or magnetic), the details of which depend on the relevant domain switching mechanisms. In the case of ferroelectricity, Stadler and Zachmanidis demonstrated in 1963 that domains switch in a two-step mechanism: nucleation and growth.<sup>7</sup> Ishibashi explained this behavior using the Kolmogorov method<sup>8</sup> to facilitate Avrami’s theory<sup>9</sup> of domain switching. In this model, domains are switched by the formation of small correlated nucleating sites that grow with time to form a larger domain. The framework of the Kolmogorov-Avrami-Ishibashi (KAI) model is valid only for the case of unconfined substances, while it breaks down for finite geometries, such as thin polycrystalline films.<sup>10</sup>

In the majority of ferroelectric-based applications, such as in random access memory devices (FeRAMs), the ferroelectric materials involved are in the form of thin polycrystalline films. For this reason, Duiker *et al.* developed an extension to the KAI switching model for finite grains.<sup>11</sup> Specifically, they showed that the relationship between the switching time constant  $t$  and

the domain correlation length  $L$  is given by

$$t = \frac{\ln 10}{RL^D}, \quad (1)$$

where  $R$  and  $D$  are the nucleation rate and dimensionality of the host material, respectively.

A major challenge for FeRAMs is to overcome retention issues, i.e., deterioration in device performance over time due to depolarization of the ferroelectric domains. In the 1990s Scott proposed that this occurs due to spontaneous nucleation of domains at the grain boundaries,<sup>12</sup> which Gruverman *et al.* verified experimentally using piezoresponse force microscopy (PFM).<sup>13–15</sup> Moreover, they found evidence of the correlation of the macroscopic polarization distribution (ferroelectric domains) between neighboring grains. However, the experimental difficulties (due to resolution and signal-to-noise issues with PFM) associated with studying the mutual influence of ferroelectricity and ferroelasticity prevented the complete understanding of the coupled switching mechanism in granular films. Hence, Gruverman *et al.* concluded that the reason for the tendency to switch along the grain boundary was not clear and needed further study. In fact, the validity of KAI extensions to describe finite patterns cannot be taken for granted. In particular, Tagantsev *et al.* supplied both experimental and theoretical arguments that challenge the correlated behavior of ferroelectric domains in confined geometries.<sup>16</sup> As a result of this, diverse alternative non-KAI models emerged,<sup>17</sup> while it is interesting to note that in some systems, the domain switching displays characteristics of both KAI and non-KAI behavior simultaneously.<sup>18</sup> In comparison with ferromagnetism, it should be noted that in confined geometries, the nature of ferromagnetism changes due to configurational anisotropy. That is, Bloch domain walls become unstable when the exchange length is comparable to the structure’s dimensions, and hence are replaced by Néel

walls. Yet, the switching mechanism involving nucleation followed by growth has recently been observed directly for the case of thin ferromagnetic films.<sup>19</sup>

Ferroelectric materials that change crystal class at the Curie temperature also exhibit ferroelasticity.<sup>20,21</sup> Therefore, the strong interplay between the macroscopic polarization and non-180° domains (i.e., between ferroelectric and ferroelastic domains) suggests that in order to fully understand either, we must take both into account. Hence, a lot of effort is still being put into dismissing the uncertainties associated with nucleation and switching mechanisms within ferroelectric-ferroelastic systems, raising questions about the validity of the KAI model.<sup>22</sup>

In ferroelectric-ferroelastic biferroic materials, ferroelastic domains are arranged as alternating out-of-plane/in-plane striped domains, i.e., periodic  $a$ - $c$  domains in the case of tetragonal structures. On the other hand, ferroelectric domains alternate by 180°, typically out of plane, but not necessarily. Recently, enhancement of the piezoresponse force microscopy technique (EPFM) has allowed high quality imaging of the behavior of both ferroelectric and ferroelastic domains simultaneously.<sup>4</sup> This has allowed a better understanding of the fact that in real materials, the alternating ferroelastic domains are not infinitely coherent. Rather, they appear in localized bundles, where the striped domains in each bundle have a well-defined orientation and periodicity. Moreover, these bundles are confined by a mesoscopic domain wall, so that these bundles constitute metaelastic domains, higher in hierarchy than the periodic domains.<sup>23</sup> It is interesting to note that bundle domains exist in many biferroic materials, and although they were first reported in the late 1940s,<sup>23</sup> they have been classified as an independent type of domain only recently.

The out-of-plane (in-plane) polarization of the  $c$  domains ( $a$  domains) within a bundle domain is usually homogeneous. These bundle domains are the building blocks of the macroscopic polarization. As a result, they play a key role in determining the stability and dynamics of the polarization states that are so important from a device point of view.<sup>24–26</sup> For instance, it has been demonstrated that application of an external electric field changes not only the polarization, but also the bundle domain distribution.<sup>24,27,28</sup> Likewise, it was found that ferroelectric domain relaxation relies upon the stability of bundle domains, which in turn exhibits a strong dependence on the local geometry of structures.<sup>24</sup>

Therefore, direct observations of bundle domain switching in finite patterns are expected to illuminate the coupled ferroelectric-ferroelastic domain switching mechanism.

The strong influence of the ferroelectric-ferroelastic bundle domains on polarization stability suggests that controlling these domains may help overcome certain key device-related problems, such as retention and fatigue (deterioration in device performance with increasing usage cycles).<sup>29</sup> One generic way to control bundle domains is through controlling the geometry of the confining structure. For instance, it has been found that alignment of the stripes not parallel to the crystallite boundary is an energetically preferable state.<sup>23,25</sup> A typical bundle domain distribution in polycrystalline ferroelectric films is demonstrated in Fig. 1.

It should be noted that in addition to sample design, a partial dynamic control of bundle domains has already been demonstrated. This is achieved for polarization field closure accompanied by a ferroelastic vortexlike structure in one of two independent mechanisms. Balke *et al.* demonstrated the ability to “drag” the domains with a moving electric field that is induced by a scanning PFM tip,<sup>28</sup> while we showed that such control can be achieved via the relaxation of purposely (electrically) cluttered nanodomains.<sup>30</sup> In fact, recently, Vasudevan *et al.* demonstrated that our model is valid also for mechanically cluttered nanodomains,<sup>31</sup> while it is interesting to note that a similar mechanism was also demonstrated for ferromagnetic vortices.<sup>32</sup> Nevertheless, a universal mechanism for controlling domain switching has still to be discovered.

In order to study the dynamics of ferroelectric-ferroelastic bundle domain switching in 190-nm-thick polycrystalline  $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$  (PZT) films,<sup>4,14</sup> we performed the following experiment. First, we imaged with PFM an area that contains a large grain (i.e., one with a diameter larger than the film thickness) with a dominant bundle domain [highlighted with a black line in Fig. 2(a)], and a small bundle. Then, we excited the domains to obtain partial switching by scanning the area while applying between the tip and the bottom electrode a dc voltage of 10 V, greater than the approximately 3-V coercive value (it should be noted that application of a voltage with the opposite polarity did not change the domain structure). As a result, two small bundle domains (which we will refer to as “nucleators”) emerged at opposite boundaries of the grains [designated by lines in Fig. 2(b)]. Finally, we excited the

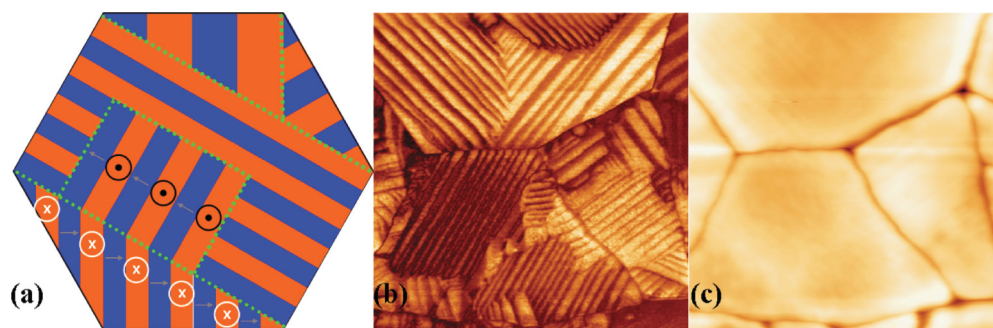


FIG. 1. (Color online) Bundle domains in ferroelectric-ferroelastic materials. (a) Schematics of bundle domains within a crystallite. The dotted lines illustrate boundaries between different domains. (b) EPFM amplitude image demonstrates bundles of periodically alternating parallel ferroelastic striped domains within a  $1.2 \times 1.2\text{-}\mu\text{m}^2$  area in a PZT film. (c) Topography of the same area.

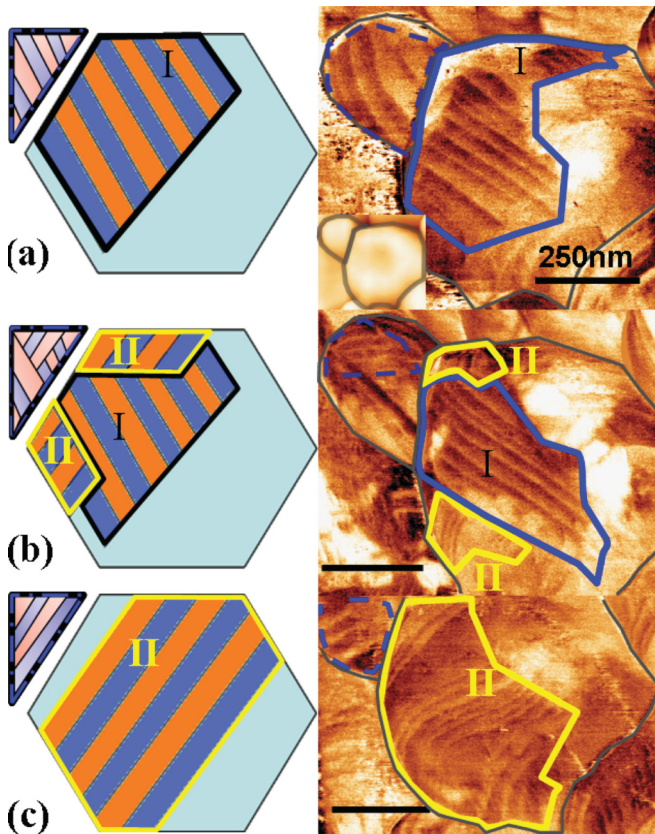


FIG. 2. (Color online) Bundle domain nucleation and growth with in-phase PFM. Schematics (left) and in-phase PFM images (right) of the switching process. (a) Native domain distribution demonstrates dominant bundle domain in a large grain (inside the blue line). Inset is topography. (b) Application of external electric field emerged small bundle domains at the grain boundaries (highlighted with yellow lines), while shrinking the original domain (within the blue polygon). (c) Repeating excitation merged the growing small domains, completing the switching of the entire bundle domain (designated by a yellow line). Dashed blue lines follow the bundle domain evolution in the top left grain, demonstrating its tendency to align in parallel to the large grain domains. Dark gray lines denote the grain boundaries. Scale bars are 250 nm.

area again in the same way, with the result that the entire original bundle domain switched to the same orientation as the previously formed nucleators [Fig. 2(c)].

There are two main results from this experiment. The first is that ferroelectric-ferroelastic domains in thin polycrystalline films can be switched via a two-step process. It starts with nucleation of small bundle domains. These nucleators form at the grain boundaries, perpendicular, or at least not parallel, to the geometrical edge. When the excitation is continued, these seeding domains grow to engulf the entire grain, completing the domain switching. These findings comply with the idea that grain boundaries can be considered as primary domain walls, from which secondary domain walls nucleate and grow.<sup>33</sup>

The second outcome is that distant nucleators can grow so that they coincide and form a single large domain. The typical coherence length (i.e., the separation or correlation length over which such nucleators can interact) can be estimated as the

distance between the two seeding bundle domains, which in this particular case is  $L \approx 500$  nm.

Following Eq. (1), if we substitute this value, as well as the typical values for PZT films:  $R = 7 \times 10^{28} \text{ s}^{-1} \text{ m}^{-3}$  and  $D = 3$ , we obtain  $t \approx 265$  ps. This result is in extremely good agreement with the experimental data obtained by Larsen *et al.*,<sup>34</sup> and by Dey,<sup>35</sup> who showed that the fastest time switching in PZT films is around 280 ps. Hence, our results are consistent with the KAI-based Duiker model for domain switching.<sup>11</sup>

The fact that the correlation length ( $L$ ) can be larger than the grain size ( $d$ ) suggests that domains of neighboring grains can interact with each other. Indeed, Gruverman *et al.* suggested more than a decade ago that the out-of-plane polarization depends on the correlated behavior of neighboring grains and hence influences ferroelectric domain switching.<sup>15</sup> This idea was then supported by independent simulations.<sup>33,36</sup> In a previous work, we studied different mechanisms of correlated behavior for ferroelectric-ferroelastic domains that span several grains.<sup>37</sup> A similar correlation mechanism for neighboring grain domains has also been deduced from direct observations of static ferromagnetic domains within neighboring crystallites by Harrison *et al.*<sup>38</sup>

An examination of the results shown in Fig. 2 indicates that such a correlation between the domains can also be seen in the above experiment. One can see that the bundle domain in the small top-left grain in the examined area (highlighted with a dashed line in Fig. 2) was also switched during the experiment. In the native state, the striped domains in this grain were oriented parallel to the adjacent bundle domain in the larger grain. Similarly to the bundle domain within the larger grain, the application of an external electric field switched these stripes. In particular, in the last part of the experiment, when the bundle domain of the large grain completed switching, the striped domains in the smaller grain re-oriented to align parallel to this switched domain. That is, the above experiment demonstrates a direct observation of the capability of domain correlation to span several grains.

In general, when the out-of-plane polarization is switched by an external electric field, the bundle domains that support the macroscopic polarization reorient in random directions<sup>24,27</sup> (with the exception of the ability to form a field closure<sup>28,30,31</sup>). Nevertheless, the significance of bundle domains to the macropolarization and to the electromechanical coupling in biferroic materials raises the need to obtain a better control of their switching. Therefore, there is a great interest in implementing the knowledge obtained from the above experiment for designing smart systems with controllable switching of these domains. The key idea behind such designs lies in the fact that first, striped domains parallel to the boundary of crystallites are unstable, and second, these domains are switched via nucleation at the grain boundary. Another important property of bundle domains that should be taken into account is that when switched in unconfined structures, switched domains tend to break into smaller bundles. On the other hand, in confined geometries, domains tend to reorient *en masse* without forming smaller bundles.<sup>23</sup> Figure 3(a) shows the geometry of a grain, in which we attempted to demonstrate controllable switching of bundle domains. The domain distribution is shown in the PFM image in Fig. 3(b),

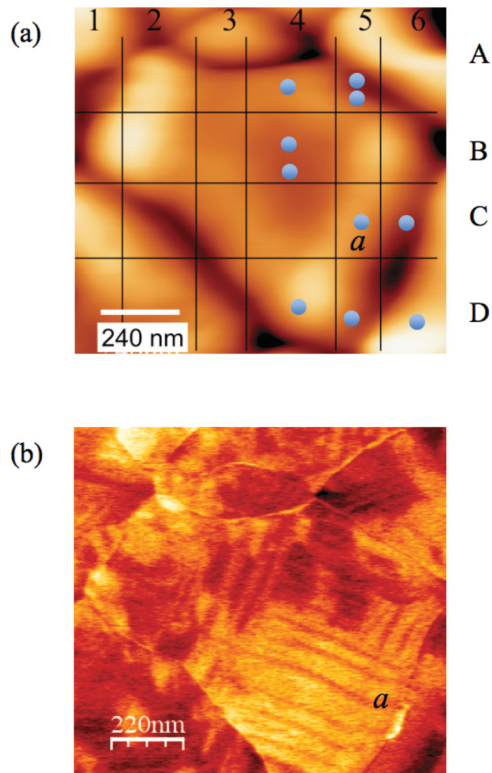


FIG. 3. (Color online) (a) Topography of area showing grain where reversibility experiments were carried out (positions indicated by spots); (b) PFM image of same area. “a” denotes an area where the ferroelastic domains are perpendicular to a grain boundary.

and again in Fig. 4(a). To obtain such controllability, the first step is to demonstrate the stability of striped domains perpendicular to the grain boundary. An area of the sample where such stripes occur naturally (area “a,” with grid reference 5C) was scanned while applying a dc voltage of 10 V, higher than the coercive value. As Fig. 4 shows, with ten subsequent domain manipulations carried out at different locations around the grain, the bundle orientation in region *a* always remained the same, even though it changed in other regions, indicating that this is indeed the most stable configuration—ferroelastic domains prefer to be perpendicular to any grain boundary they encounter.

As illustrated in Fig. 3(b), the trapezoidal shape of the grain enforces the striped domains that are perpendicular to one boundary (on the right) to be almost parallel to another boundary (at the bottom). This means that the ferroelectric-ferroelastic domains close to the bottom boundary should be less stable and can be excited rather easily to reorient perpendicular to this boundary. Hence, we scanned this area by applying 10 V between the tip and the sample. As a result, indeed, the bundle domain was switched, reorienting its stripes perpendicular to the bottom grain boundary [Fig. 4(d)]. It should be noted that further excitation of the switched stripes in the same area did not affect them, indicating that this is indeed the most stable configuration here. In order to demonstrate reversible control of the domain switching, one must demonstrate that the rotated domains can be switched back to their original state, which can be accomplished by controlling where the nucleation occurs. When these domains were switched,

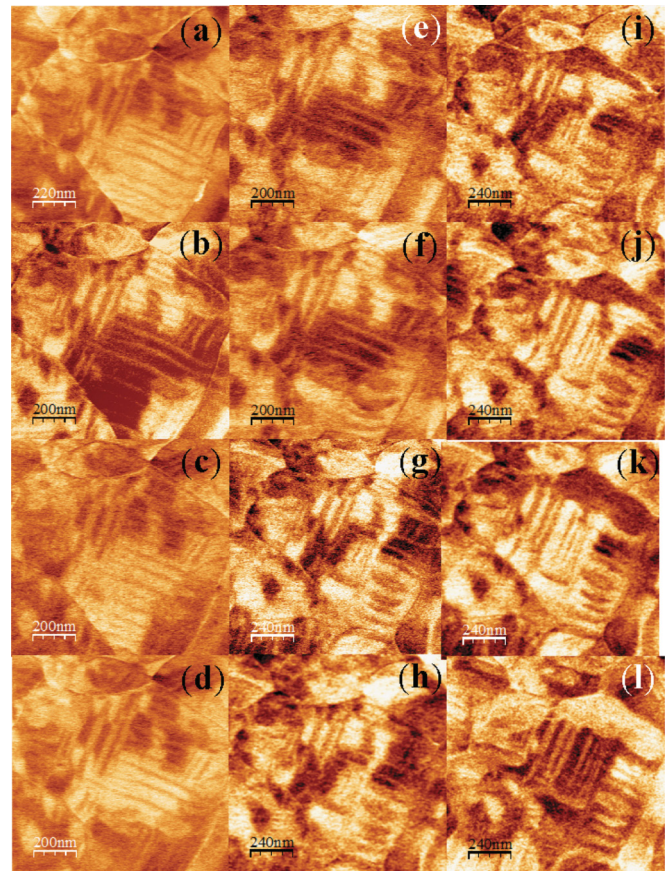


FIG. 4. (Color online) Ferroelectric-ferroelastic domain engineering. In-phase PFM images of the area shown in Fig. 3, after different zones were scanned at a voltage higher than the coercive value. (a) Native domain distribution. (b) After 5C was written. (c) After writing 6C. (d) After writing 4D. (e) After writing 6D. (f) After writing 5D. (g) After writing 4B (at the *a-a* junction). (h) After writing 5A. (i) After writing 4A. (j) After writing 4B (at the *a-a* junction). (k) After writing 5A. (l) After writing the entire area. Arrows indicate the center of the areas that were “written.”

they also became parallel to the right-hand-side boundary of the grain, which will be unstable. Therefore, by exciting the domains around the right-hand-side grain boundary, it is expected to reverse the switched domain so that the stripes will return to the original configuration. Figure 4(f) shows that the excitation did reverse the domain switching so that the stripes returned to their original orientation successfully. Therefore, in this experiment we have demonstrated that by taking advantage of the geometry of grains, one can use the stability of striped domains that are perpendicular to the grain boundary and the high-energy state of stripes parallel to the grain boundary for switching ferroelectric-ferroelastic bundle domains reversibly at will. Since bundle domains couple the electrical properties (e.g., macroscopic polarization and response to electric field) to the mechanical properties (strain and stress), such controllable switching may assist overcoming technological problems such as fatigue and retention. Further experiments where we applied local electric fields to alter the domain configuration are shown in Figs. 4(g)–4(k). It is clear from these data that the most stable configuration is one where within a single grain with complex geometry, what may start

off as a single domain splits into a number of bundle domains at  $90^\circ$  to each other, to achieve near perpendicularity with adjacent grain boundaries. Further application of local or even global electric fields [Figs. 4(k)–4(l)] no longer makes any difference as this domain configuration is already the most stable one.

To conclude, in the current paper we discussed the mesoscale behavior of ferroelectric-ferroelastic domains in thin polycrystalline PZT films. We studied the switching mechanism of such domains, demonstrating that this can involve nucleation and growth. That is, when external excitation is introduced, small bundle domains arise at the crystallite boundaries. As the excitation progresses, the small bundle domains act as nucleators that grow until they meet and form the new (switched) domain. We found that the nucleator's coherence length in the examined samples is  $\sim 500$  nm and

that domains can interact with each other even if they are located in different crystallites. Moreover, we discussed how these findings comply with the KAI-based Duiker's model for domain switching in polycrystalline thin films.<sup>11</sup> While our results do not offer a validation of the model, they at least do not rule it out. Further observations on the propagation of domain walls will be needed to elucidate the mechanisms behind domain switching. Last, based on our understanding of the switching mechanism, we postulated and demonstrated a method for controlled domain engineering that is based on geometrical design of the confining structure.

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\*Corresponding author: yachinivry@gmail.com

†Corresponding author: cd229@eng.cam.ac.uk

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