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A Perspective on Conducting Domain Walls and Possibilities for Ephemeral Electronics

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Abstract

This “perspectives” article briefly summarises what is known about electrically conducting domain walls. It highlights insights into the underlying causes of enhanced current transport, developed despite the frustrations and limitations of the standard two-probe source and drain measurements that have dominated the field to date (because of the pervasive use of conventional conducting Atomic Force Microscopy). The article gives a feel for the unique possibilities offered by conducting domain walls, in future forms of agile electronics. Indeed, it is imagined that domain walls and domain wall junctions might eventually allow for entire nanoscale circuits (devices and their interconnects) to be created in one instant, for one purpose, only to be wiped clean and rewritten in a different form, for a different purpose, in the next instant. Malleable domain wall network architecture, that can continually metamorphose, could represent a kind of technological genie, granting wishes on demand for radical moment-to-moment changes in electronic function.

I. INTRODUCTION

Somewhat remarkably, two electrically insulating materials, brought into contact, can generate a highly conducting (or even superconducting) interface where they abut. The most well-known instances occur at *heterointerfaces* between dissimilar materials, such as LaAlO_3 thin films on either SrTiO_3 or KTaO_3 single crystal substrates [1,2]. However, emergent conductivity is not the preserve of junctions between dissimilar systems; it can also arise at *homointerfaces*, involving contact between two pieces of the same material. In this second category, twin and domain walls are extremely important; in fact, some of the earliest predictions of emergent conduction at interfaces between two insulators were made specifically for these kinds of boundaries [3].

Experimental hints of homointerfacial conduction have peppered the literature for almost half a century but remained “under the radar” and their importance is, perhaps, only obvious with hindsight: in 1977, for example, Schmid and Petermann [4] reported conductivity anomalies at improper ferroelectric phase transitions, in single crystal Cu-Cl boracites. Finding differences between electrically poled and unpoled samples, they suggested “*the lower dc resistivity of unpoled samples may be due to . . . a higher conduction along the [domain] walls*”. Unequivocal measurements were first published by Aird and Salje in 1998 [5], finding superconductivity along walls in reduced $\text{WO}_{3-\delta}$ crystals. For some reason, though, this work did not resonate strongly at the time. In fact, it was not until 2009 that the consciousness of the functional oxides research community was properly awakened, through the discovery of leaky domain walls in BiFeO_3 [6]. For most, it seems, seeing-is-believing and it is certainly true that the published conducting Atomic Force Microscopy (cAFM) maps, in which enhanced current levels at domain walls could be observed directly by any reader, had a significant impact. Since then, interest has grown steadily, as researchers have attempted to map and understand the fundamentals of conduction and explore the possibilities for creating new kinds of domain wall devices. Importantly, in almost all cases, homointerfacial conducting domain walls are found in ferroelectric materials.

II. TRANSPORT PHYSICS OF CONDUCTING DOMAIN WALLS

Although cAFM images were crucial for igniting wider interest in the topic, the technique has been a bit of a mixed blessing. On the one hand, cAFM has allowed the research community to discover conducting domain walls across a range of ferroelectric materials

rather easily: from perovskite or perovskite-like oxides [6-9] to rare-earth manganites [10,11], boracites [12,13] and Ruddlesden-Popper systems [14]. In addition, because cAFM and piezo-response force microscopy (PFM) can readily be done on the same microstructural region, the technique has allowed the importance of domain wall polarisation discontinuities, for enhanced conductivity, to be clearly revealed [10,15]. On the other hand, the fact that the basic operation of cAFM only involves 2-probe current measurement (with the source or drain being the conducting AFM tip) has meant that attempts to probe fundamental domain wall transport physics have been frustrated by the dominating barrier resistance associated with the electrode-sample contact: almost without fail, domain wall currents, examined as a function voltage and temperature, have ended up mapping either Simmons-Richardson-Schottky [7, 16-18] or Fowler-Nordheim [19] barrier characteristics. It is true that some studies have deliberately used the tip-sample barrier imaginatively for device demonstration purposes (in domain wall-related ac rectification, for example [11]). Overall, though, this contact resistance has frustrated the field of research. Meaningful temperature variations of conductance, for example, that are definitively attributable to the domain wall only (without any barrier influence) have not been seen and “metallic-like” responses have hence only been loosely established [8,19].

Having said that, progress has been made and insights into the fundamental physics of domain wall transport have been developed. It is now believed that conduction is enabled by one or more of the following mechanisms, depending on the specific system being considered [20] (see figure 1):

- (i) *domain walls can attract and aggregate defects* (through strain-field interactions for example). Such defects can introduce extrinsic electronic states within the band-gap, creating either holes or itinerant electrons at finite temperature. BiFeO₃ domain wall conduction seems particularly influenced by such defect states [16-18, 21]. It seems their presence can facilitate transport even at low temperature, where there is growing evidence of carrier hopping between mixed-valence Fe³⁺-Fe⁴⁺ ions [22,23]. In addition, if the defects themselves are mobile and charged, then they can provide the possibility for direct ionic transport.
- (ii) *the electronic structure of domain walls can differ from that of the bulk material*, as the crystallographic environment at the wall is distinct; evidence

- exists for band-gap alterations (reductions) from both atomistic simulations [24] and direct measurement (using scanning tunnelling spectroscopy [25]).
- (iii) *the entire band-structure of the bulk material can be locally depressed or elevated in absolute energy terms* (in comparison to the vacuum). For example, for those at which polarisation vectors point towards each other (head-to-head walls), the near-fields associated with positive interfacial bound charge will stabilise (reduce the energy of) electron states and may even depress the band structure to such an extent that the conduction band may dip below the Fermi Level, within the domain wall, to cause a local accumulation of free electrons. Similarly, where polarisation vectors point away from each other (tail-to-tail walls), the band structure energy will increase and this may allow the top of the valence band to rise above the Fermi Level, creating local hole carriers.

Magnetotransport behaviour has also been mapped to some degree [22,26-29]. In BiFeO₃ walls (the most heavily studied), significant low-temperature longitudinal magnetoresistance has been established [26], as has smoothly varying anisotropic magnetoresistance [22]: both signs of magnetic ordering in this specific material. Local Hall Voltage measurements (made using modified scanning probe microscopy techniques) have also been employed on rare earth manganite walls [28,29] and have revealed unexpectedly low densities of active carriers (many orders of magnitude lower than would be needed to screen polarisation discontinuities). Unusually high carrier mobilities have also been established. This suggests physics of spatial confinement, as enhanced mobilities are a general feature of two-dimensional electron gases (2DEGs). However, categorical evidence for this, through Shubnikov-de Haas oscillations or direct Quantum-Hall measurements, has not yet been found. There is still much work to do.

III. POTENTIAL FOR APPLICATIONS

Over the last 20 years, the exotic electronic properties of graphene, in which semiconducting, metallic and superconducting responses can all be realised, have spearheaded a tidal wave of research on 2D functional materials. In many ways, the rather late addition of conducting ferroelectric domain walls to the now long list of suspected 2D systems may therefore seem uninteresting.

However, domain walls offer something genuinely unique. Electrical bias, stress fields and variations in temperature can all cause the microstructure of ferroelectrics to change: some domains grow while others shrink; some domains disappear altogether and some, that had not previously been present, can be nucleated into existence. Microstructural changes can be site-specifically controlled and, consequently, in principle, domain walls can be created, moved and annihilated at will [30-32]. The possibilities afforded by controllable “now-you-see-it-now you-don’t” mercurial conducting domain wall conduits for new kinds of devices were noted in Siedel *et al.*’s seminal work [6], where a proof-of-concept memristor was even explicitly demonstrated: conduction states were varied by writing different numbers of domain wall channels between source and drain electrodes using a conducting AFM tip. More operationally pragmatic domain wall memristors [33-36], transistors [37] and binary memory bits [38,39] have since been developed and their potential applications are growing (in neuromorphic circuitry, for example).

Mobile conducting walls have also prompted notions of reconfigurable nanocircuitry, as has been nicely conveyed by Nava Setter and her research team, in a 2017 youtube video [40]. Here, the thesis is that the passive components in a circuit might be fixed (in the analogy used, like the buildings in a futuristic city), but the domain wall interconnects (or roads in the city) could be repositioned dynamically to change overall circuit characteristics (or the way in which the city logistics might function). Figure 2 is a still frame from the video, illustrating the possibilities offered by rewriting the road networks between buildings and attractions in the notional city considered.

While inventive, both the creation of individual devices and the idea of reconfigurable interconnects, as described above, may only be limited versions of a more ambitious and dramatic future vision for domain wall electronics: the coexistence of head-to-head and tail-to-tail walls, within the same microstructure, means that both n and p -type transport could simultaneously exist in arrays of 2D conducting networks. Where head-to-head and tail-to-tail domain walls intersect or meet, 1D p-n junctions should be expected and so in-wall diodes, transistors and logic gates could, in principle, be made. Moreover, the fact that domain walls can be created, moved and annihilated means that entire chips could be formed inside a block of ferroelectric one moment, for one purpose, and then erased and completely redesigned and reformed for a different purpose in the next. Changing or ephemeral electronics (“chameleon” electronics perhaps), where both interconnects and

devices are transient in nature, but dynamically controlled, might hence be the ultimate dream.

It is not complete fantasy either. In ErMnO_3 , for example, Dennis Meier and coworkers have established that both head-to-head (presumed n -type) and tail-to-tail (confirmed p -type) charged domain walls can conduct, if sufficient driving voltages are applied [41]. In addition, six-fold domain wall junctions are characteristic of the microstructures found in these systems: head-to-head and tail-to-tail (n and p -type) walls therefore inevitably meet and 1D p - n junctions are hence suspected to form (although their full electrical characterisation still needs to be done). Figure 3 illustrates both the junctions and their interconnected nature, as well as the possibilities for logic gates, for example. Admittedly, the domain wall microstructure in the manganites is not as malleable under applied external fields as is the case for other ferroelectric systems (the six-fold domain wall junctions are “topologically protected” – all six domain variants are needed for lattice continuity). Nevertheless, the manganites point the way towards the opportunities of combining current-carrying p and n -type domain walls with domain wall junctions and must prompt us to discover other systems, where the domain walls and junctions can be moved and reconfigured more easily.

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Figure 1: (reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature Reviews Physics **2** 634 (2020). Copyright 2020, Springer Nature Limited) There are three primary mechanisms proposed which may be responsible for enhanced electrical conduction along ferroelectric domain walls. Firstly **(a)**, point defects might aggregate at domain walls, to reduce the combined wall and point defect energy cost. Such defects could introduce extrinsic electronic states within the bandgap. Secondly **(b)**, as the atomic environment at the domain wall is different from bulk, the local electronic structure could also differ, to potentially cause a band-gap reduction. Thirdly, polarisation discontinuities present at “charged” walls may shift the absolute energy of the band-structure of the bulk material at the domain walls relative to the vacuum, to either allow the conduction band to dip below the Fermi Level, or the valence band to poke above it **(c)**. There is experimental evidence to support all three of these mechanisms.

Figure 2: (still frame taken from reference [40] with permission from EPFL Mediacom)
One of the possibilities for domain wall electronics is that conducting walls could be used to make, break and then change the connections between fixed devices in reconfigurable electronic circuits. In [40], this notion is likened to changing the road network in a city to alter the logistics of how the city might function.

Figure 3: $\sim 25 \times 30$ square micron area lateral piezoresponse force microscopy (PFM) amplitude (a) and phase (b) images of an ErMnO_3 single crystal slice, with its polished surface parallel to the uniaxial polarisation axis (the scanning probe cantilever axis is horizontally oriented). Different regions of charged domain walls can be identified (c) across which there are discontinuities in the polarisation, either denoted as “head-to-head” (H-to-H) or “tail-to-tail” (T-to-T). In ErMnO_3 , both types of charged domain walls can display enhanced conductivities in comparison to the bulk domains. Many junctions can be seen, where p-type T-to-T and suspected n-type H-to-H walls meet. The functional possibilities for connected arrays of 1D p-n junctions (marked with dots and circles in the microstructure) are self-evident. It is tantalising to imagine that such networks might lead to the possibility of n-p-n or p-n-p domain wall transistors or at least diode-based logic gates (d).