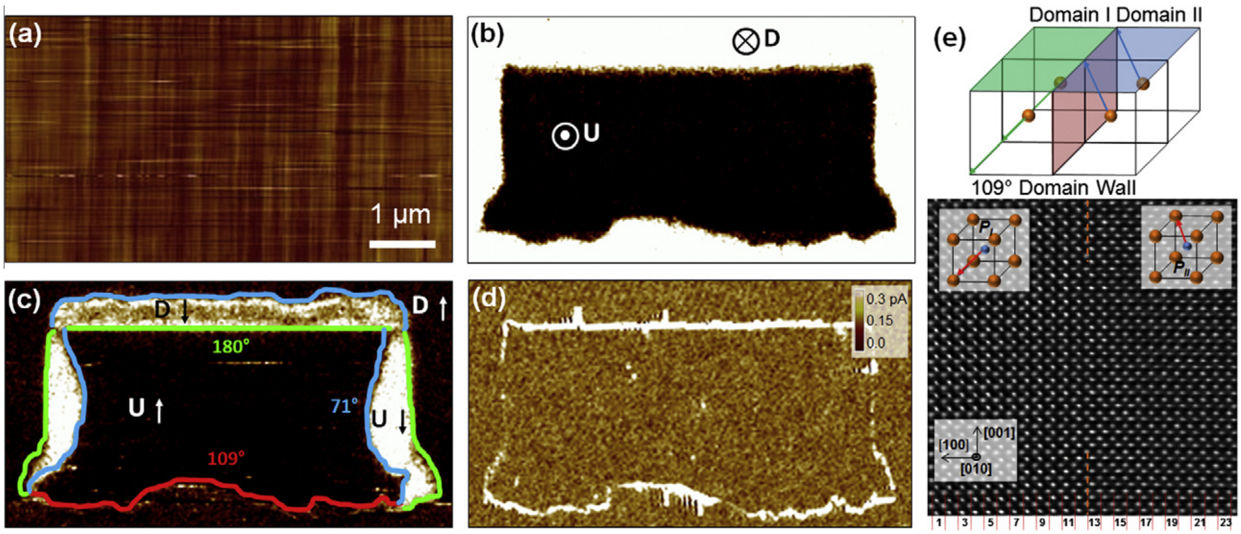

Fig. 5. Conduction at domain walls in $BiFeO_3$. (a) Topographic image of the surface of a model $BiFeO_3/SrRuO_3/SrTiO_3$ (1 1 0) sample as image via atomic force microscopy. Corresponding out-of-plane (b) and in-plane (c) piezoresponse force microscopy images of a switch portion of the same film. Domain wall types and locations are labeled. (d) Conducting-atomic force microscopy image of switched portion of the film reveals certain types (name 109° and 180° domain walls) that conduct. (e) Schematic illustration of a 109° domain wall and corresponding high-resolution transmission electron microscopy image of a 109° domain wall. Analysis reveals the presence of a net polarization perpendicular to the domain wall and a change in the local structure at the domain wall – both of which could give rise to enhanced conduction (adapted from Ref. [63]).

found that the normal component of the polarization showed a small increase in the vicinity of the domain wall. Calculations indicated that this small change in the normal component of the polarization across these domain walls could lead to a step in the electrostatic potential (planar and macroscopically averaged) of 0.15–0.18 eV across the domain wall, similar to a step computed previously for 90° domain walls in $PbTiO_3$ [64]. Such a potential step should enhance the electrical conductivity by causing carriers in the material to accumulate at the domain wall to screen the polarization discontinuity. Additionally, the change in the structure (trending towards higher symmetry) could also result in a narrowing of the band gap for this material. It was noted that both situations are the result of the same structural changes at the wall and both may, in principle, be acting simultaneously, since they are not mutually exclusive.

3.4. Magnetoelectric coupling in $BiFeO_3$

Although many researchers anticipated strong magnetoelectric coupling in $BiFeO_3$, until the first evidence for this coupling in 2003 there was no definitive proof. Three years after this first evidence, a detailed report was published in which researchers observed the first visual evidence for electrical control of antiferromagnetic domain structures in a single phase multiferroic at room temperature. By combining X-ray photoemission electron microscopy (PEEM) imaging of antiferromagnetic domains (Fig. 6a and b) and piezoresponse force microscopy (PFM) imaging of ferroelectric domains (Fig. 6c and d), they were able to directly observe changes in the nature of the antiferromagnetic domain structure in $BiFeO_3$ with application of an applied electric field (Fig. 6e) [65]. This research showed that the ferroelastic switching events (i.e. 71° and 109°) resulted in a corresponding rotation of the magnetization plane in $BiFeO_3$ (Fig. 6f) and has paved the way for further study of this material in attempts to gain room temperature control of ferromagnetism (to be discussed in detail later) and has since been confirmed by neutron diffraction experiments in bulk $BiFeO_3$ as well [66].

3.5. Horizontal multilayer heterostructures

An alternative approach to obtain a magnetoelecric effect is through multilayered heterostructures. Great strides have been made in the area of composite magnetoelectric systems. These systems operate by coupling the magnetic and electric properties between two materials, generally a ferroelectric material and a ferrimagnetic material, via the lattice (i.e. piezomagnetism couples to piezoelectricity). An applied electric field creates a piezoelectric strain in the ferroelectric, which produces a corresponding strain in the ferrimagnetic material and a subsequent piezomagnetic change in magnetization or the magnetic anisotropy. Work started in the field several decades ago using bulk composites, although experimental magnetoelectric voltage coefficients were far below those calculated theoretically [67]. In the 1990s theoretical calculations showed the possibility for strong magnetoelectric coupling in a multilayer (2–2) configuration; an ideal structure to be examined by the burgeoning field of complex oxide thin-film growth [68]. In this spirit, researchers experimentally tested a number of materials in a laminate thick-film geometry, including ferroelectrics such as $Pb(Zr_x,Ti_{1-x})O_3$ [69–74], $Pb(Mg_{0.33}Nb_{0.67})O_3$–$PbTiO_3$ (PMN–PT) [75], and ferromagnets such as $TbDyFe_2$ (Terfenol-D) [69], $NiFe_2O_4$ [70,72], $CoFe_2O_4$ [74], $Ni_{0.8}Zn_{0.2}Fe_2O_4$ [71], $La_{0.7}Sr_{0.3}$