doi:10.1017/S1431927621002907
Microsc. Microanal. 27 (Suppl 1), 2021

Direct observation of polarization-induced two-dimensional electron/hole gases at ferroelectric-insulator interface

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Two-dimensional electron gas or hole gas (2DEG or 2DHG) and their functionalities at artificial heterostructure interfaces have attracted extensive attention in recent years. Many theoretical calculations and recent experimental studies have shown the formation of alternating 2DEG and 2DHG at ferroelectric/insulator interfaces. When the polarization points toward the interface, additional electrons will move toward the interface to screen the positive polarization bound charge, resulting in an increased charge density of electrons and forming 2DEG. But when the polarization points away from the interface, electrons are pulled away from the interface, reducing the electron charge density and forming 2DHG. This has been predicted in $BaTiO_3/SrTiO_{31}$ and $PbTiO_3/SrTiO_{3.2}$ Experimental studies have shown indirect evidence indicating the existence of two-dimensional free-carrier gases at BFO/$TbScO_3$ $(TSO)_3$ interfaces using conductive atomic force microscopy (C-AFM) and electron energy loss spectroscopy (EELS), supported by theoretical calculations. However, there has not been a direct measurement of the local charge distribution in the 2DHG/2DEG.

Here, we studied the charge distribution at a BFO/TSO interface using atomic resolution STEM, EDS, 4D STEM4, and Bader charge analysis, and demonstrate the build-up of 2DHG/2DEG that is induced by upward (points away from the interface)/downward (points toward the interface) polarization. In Fig 1, an atomic resolution STEM shows the cross-sectional view of the BFO film with ordered 109° domain arrays, and the atomic-resolution EDS reveals that the BFO's termination layer is Fe-O_2. To investigate the possible existence of 2DHG or 2DEG at the BFO/TSO interface, we measured the total charge of each Fe/O column by performing 4D STEM and Bader charge analysis on the BFO side from the regions in Fig 1d and e and the results are shown in Fig. 2a and b. The positive nuclei, screened by the core electrons appear as positive charges in the charge density map, while the valence electrons appear as negative charge between the atomic columns. Each Fe/O column is defined by a black rectangle box by finding the local minima of the charge density, including both the nuclei and the surrounding electrons. By averaging the total charge of each unit cell row, the measured charge on Fe/O columns for the upward and downward polarization states as a function of a distance from the BFO/TSO interface are plotted in Fig. 2c. For the interfaces with upward polarization state, the measured charge on 0th and 1st (0th: ~ 0.18e, 1st: ~ 0.22e) unit cells are higher than that on the subsequent 8 layers (~ 0.3e) which are far away from the interface, indicating a build-up of 2DHG. For the interfaces with downward polarization state, the measured charges on first two unit cells (0th: ~ 0.18e, 1st: ~ 0.22e) are lower than the rest (~ 0.3e) and the charge in the first three unit cells increases moving away from the interface, indicating there is a 2DEG.

In conclusion, by using 4D STEM and Bader charge analysis to quantify the local charge distribution, we have directly observed the build-up of 2D free electron/hole gases at the ferroelectric/insulator (BFO/TSO) interface, which are induced by spontaneous polarizations. Based on the analysis of the atomic-resolution charge density mapping, we found that the upward polarization state will induce 2DHG while downward polarization state will induce 2DEG, both within the first two unit-cells adjacent to the interface. This technique opens up a new path of directly observing charges in atomic scale, contributing to establishing the design paradigm for next-generation electronic nanodevices.

Acknowledgements

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (DE-SC0014430), and partially by the NSF under grant number DMR-2034738. TEM experiments were conducted using the facilities in the UC Irvine Materials Research Institute (IMRI), which is supported in part by the NSF Materials Research Science and Engineering Center program (DMR-2011967)

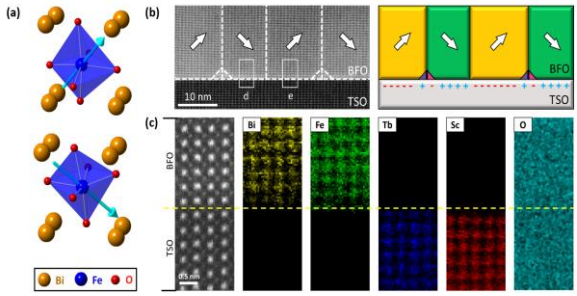

Figure 1. FIG. 1. (a) atomic models of the pseudocubic structure of BFO. Polarization are shown by cyan arrow (b) Low-magnification HAADF STEM image of a cross-section of BFO/TSO heterostructure and the corresponding schematic of the domain arrays. (c) An atomically resolved HAADF STEM image and corresponding EDS mappings of the BFO/TSO interface. (d) and (e) are the regions where Fig. 2b and Fig. 2a collected from.

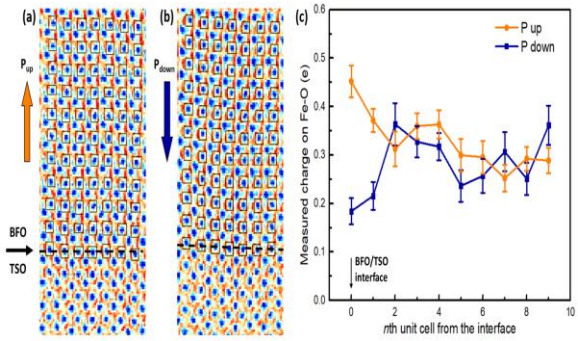

Figure 2. FIG. 2. (a) and (b) are charge density maps measured from Fig. 1 e and d, respectively, with all the Fe/O columns defined by black rectangle boxes. (c) Averaged measured charge on Fe/O columns of each unit cell row as a function of number of unit cells from the BFO/TSO interface. Red and blue arrow and dots represent upward and downward polarization states, respectively.

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https://doi.org/10.1017/S1431927621002907 Published online by Cambridge University Press