Resistive Switching Behavior in Ferroelectric Heterostructures

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Resistive Switching Behavior in Ferroelectric Heterostructures

Zhan Jie Wang and Yu Bai*

Resistive random-access memory (RRAM) is a promising candidate for next-generation nonvolatile random-access memory protocols. The information storage in RRAM is realized by the resistive switching (RS) effect. The RS behavior of ferroelectric heterostructures is mainly controlled by polarization-dominated and defect-dominated mechanisms. Under certain conditions, these two mechanisms can have synergistic effects on RS behavior. Therefore, RS performance can be effectively improved by optimizing ferroelectricity, conductivity, and interfacial structures. Many methods have been studied to improve the RS performance of ferroelectric heterostructures. Typical approaches include doping elements into the ferroelectric layer, controlling the oxygen vacancy concentration and optimizing the thickness of the ferroelectric layer, and constructing an insertion layer at the interface. Here, the mechanism of RS behavior in ferroelectric heterostructures is briefly introduced, and the methods used to improve RS performance in recent years are summarized. Finally, existing problems in this field are identified, and future development trends are highlighted.

was predicted based on the relationship between charge and flux.[4] In 2008, the Hewlett-Packard Laboratory reported that a memristor can be realized using the RS effect of TiO_2 films, which led to new research interest in the RS behavior of materials.[5]

RS behavior is typically realized through a capacitor-like structure in which an RS material is sandwiched between two electrodes.[1c,6] Currently, binary metal oxides have presented noticeable RS performances, and great breakthroughs have been made in understanding their mechanisms.[1a,2] These materials are normally insulating in the pristine state. Thus, an "electroforming" or "forming" step that applies a large voltage is usually required to develop the initially conductive pathways. However, it has been shown

I. Background about resistive switching (RS)

II. The mechanism of RS behavior in ferroelectric heterostructures

III. The methods used to improve RS performance

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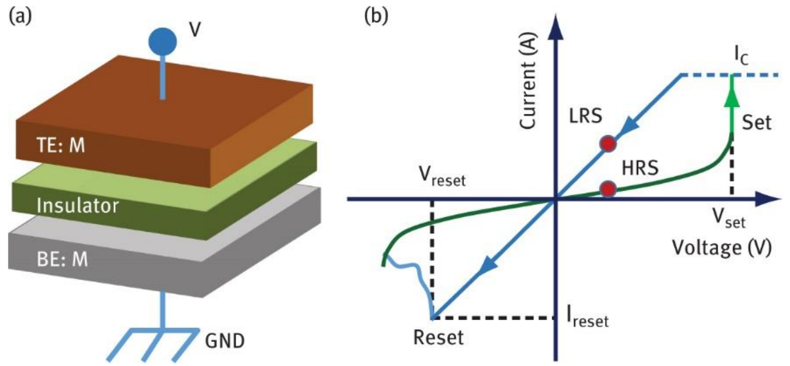
Motivation & Background

Resistive random-access memory (RRAM)

- a promising candidate for next-generation nonvolatile random-access memory protocols.

  - ✓ fast switching speed
  - ✓ low power consumption
  - ✓ nondestructive readout



- The information storage in RRAM is realized by the resistive switching (RS) effect, which is defined as the conversion of a material's resistance between a high resistance state (HRS, OFF) and a low resistance state (LRS, ON).

- These materials are normally **insulating in the pristine state**.
- Thus, an "**electroforming**" or "**forming**" step that applies a large voltage is usually required to develop the **initially conductive pathways**.
- However, it has been shown that the **chemical composition inevitably changes during the RS process**, such as the local redox reaction. Therefore, the **reliability** of the RS behavior of these materials has demonstrated problems to some extent.

Motivation & Background

Ferroelectric materials with RS effect:

1) RS behavior is related to ferroelectric polarization switching. Ferroelectric materials have spontaneous polarization, and these **polarizations can be reversed with an applied electric field**.
2) Moreover, the **remnant polarization remains stable**, even after more than 10^9 polarization reversals.
3) In addition, the ferroelectric RS behavior of ferroelectric oxides does **not require** these "electroforming" or "forming" processes

Therefore, the **stability** of the ferroelectric polarization switch is sufficient to control RS behavior

Ferroelectric RS devices

- Depends on the thicknesses of ferroelectric tunnel junctions

Ferroelectric tunnel junctions (FTJ)

A few nanometers, quantum-mechanical tunneling

Ferroelectric diodes

Tens to hundreds of nanometers

Motivation & Background

Ferroelectric tunnel junctions

- ❑ The tunnel transmission of electrons can be **modulated by the polarization direction of the ferroelectric layer**, resulting in good RS performance with an ON/OFF ratio of more than 10^4.
- ❑ The preparation of **high-quality ferroelectric ultrathin films** is of great importance to FTJs, which has hampered the limited research and application of FTJs.

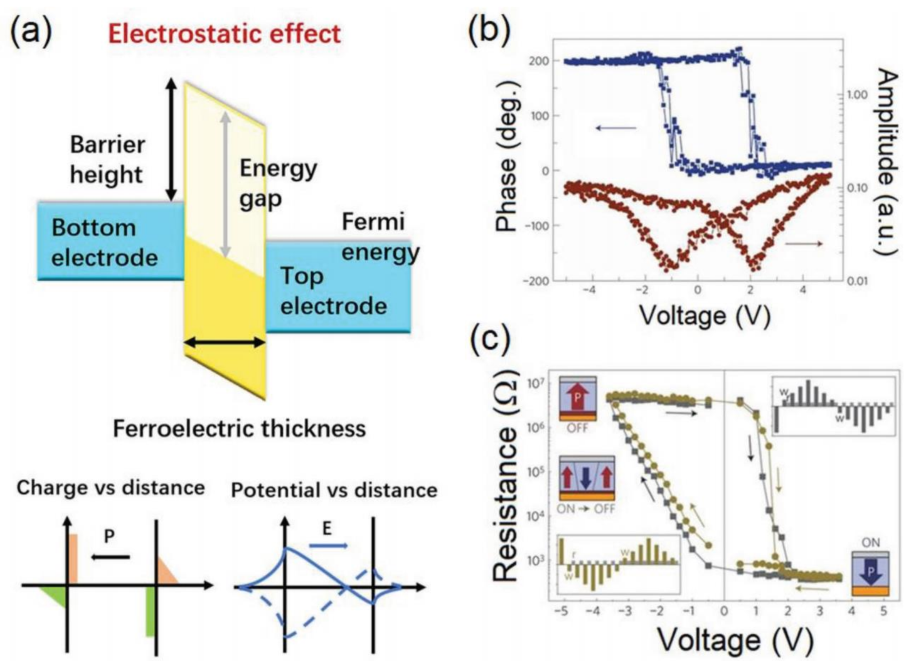


Figure 1. Ferroelectric tunnel junction. a) Schematic diagram of a tunnel junction. Electrostatic effect: charge distribution and the respective potential profile. b) Local PFM hysteresis loops of ultrathin $BaTiO_3$ films. c) Resistive hysteresis loops of $Pt/BaTiO_3/Nb:SrTiO_3$ FTJs. The dark-square (green circle) loop is measured using the pulse train shown in the bottom-left (top-right) inset. The device is preset to the ON (OFF) state by a positive (negative) 3.6 V pulse. All panels reproduced with permission.[13c] Copyright 2013, Springer Nature.

Motivation & Background

Ferroelectric diodes

- Ferroelectric thin films of tens to hundreds of nanometers can be prepared relatively easily by various methods, and **good ferroelectric properties can be guaranteed**.
- In addition, ferroelectric heterostructures consisting of a ferroelectric film and a lattice-matched oxide electrode exhibit **various intriguing physical effects** through **interfacial couplings of spin, orbit, charge, and lattice degrees of freedom**.

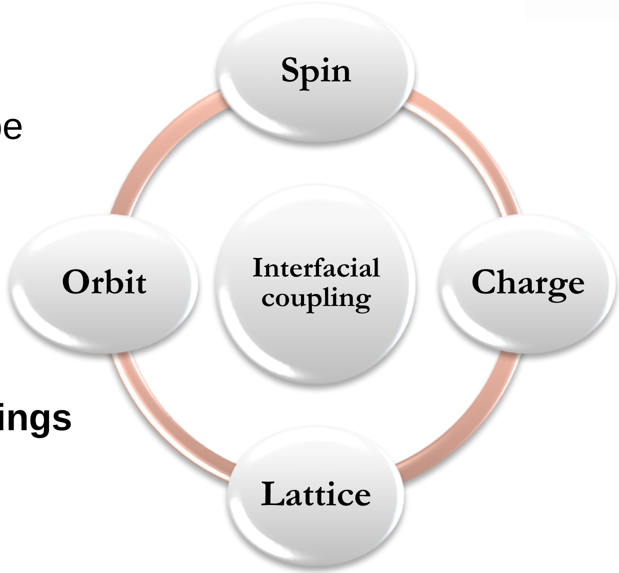


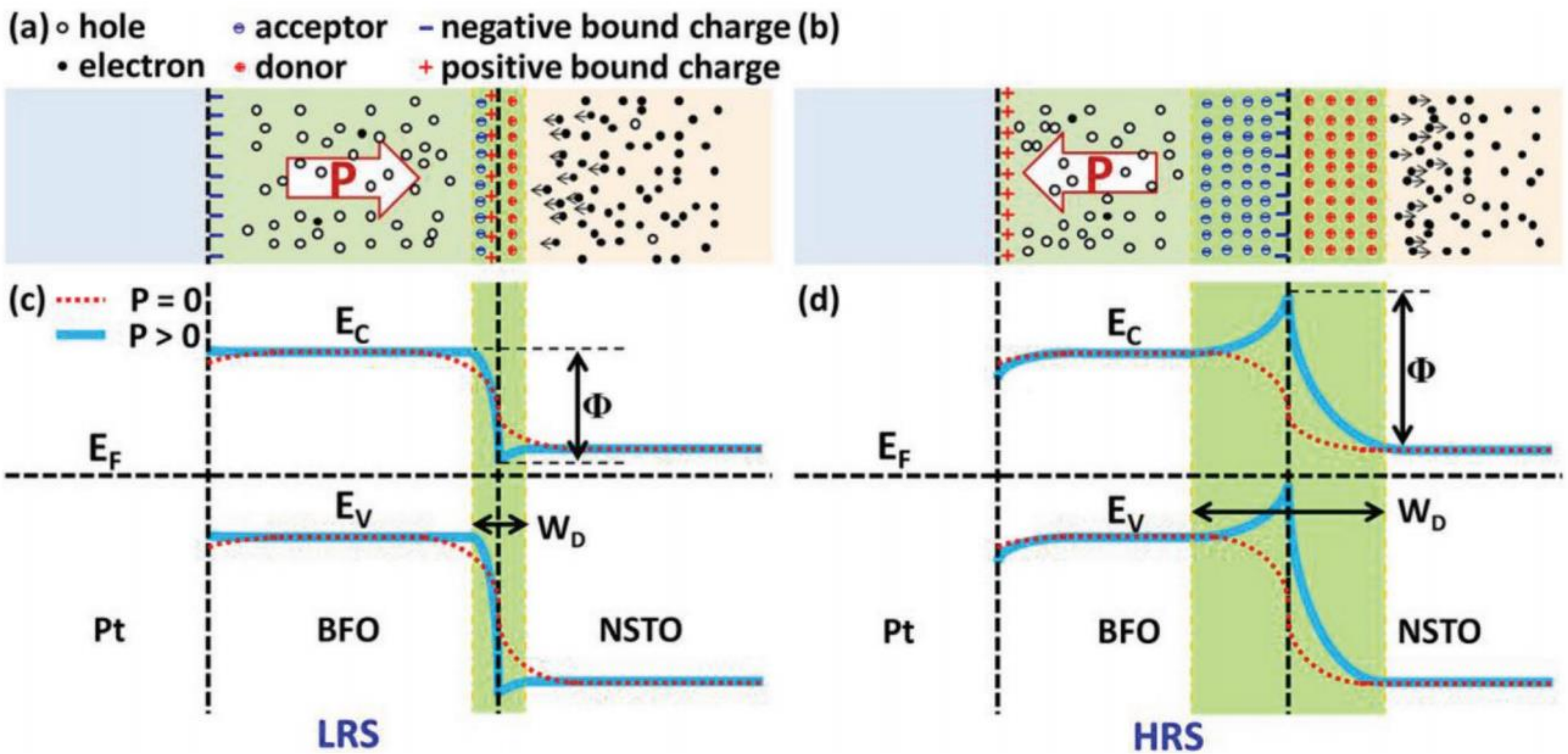
Table 1. Experimental results of RS ratio in ferroelectric heterostructures.

Heterostructures (ferroelectric/electrode)	*d*[nm]	ON/OFF	Preparation	Year	Ref.
$PbTiO_3/La_{0.5}Sr_{0.5}CoO_3$	200	100	PLD	1994	[18a]
$Ba_{0.7}Sr_{0.3}TiO_3/SrRuO_3$	40	5	PLD	2006	[19]
$BiFeO_3/SrRuO_3$	300	100	PLD	2009	[18b]
$BiFeO_3$/Nb:$SrTiO_3$	100	100	PLD	2011	[20]
$BiFeO_3/LaNiO_3$	250	1000	CSD	2012	[18e]
$BiFeO_3$/ZnO	300	1 000 000	PLD	2013	[21]
$BaTiO_3/La_{0.7}Sr_{0.3}MnO_3$	300	1000	PLD	2015	[22]
$Bi_{0.925}Sm_{0.075}Fe_{0.95}Ni_{0.05}O_3$/FTO	250	12 000	CSD	2015	[23]
$PbZr_{0.4}Ti_{0.6}O_3$/Nb:$SrTiO_3$	150	850	CSD	2016	[24]
$BaTiO_3/SrRuO_3$	60	4500	PLD	2016	[25]
$La_{0.1}Bi_{0.9}FeO_3/SrRuO_3$	88	2500	MS	2018	[26]
$PbZr_{0.52}Ti_{0.48}O_3$/Mn:ZnO	125	150	CSD	2018	[18g]

d, thickness of ferroelectric layer; PLD, pulse laser deposition; CSD, chemical solution deposition; and MS, magnetron sputtering. The reports are ordered by year.

The mechanism of RS behavior in ferroelectric heterostructures

1) Polarization-dominated mechanisms

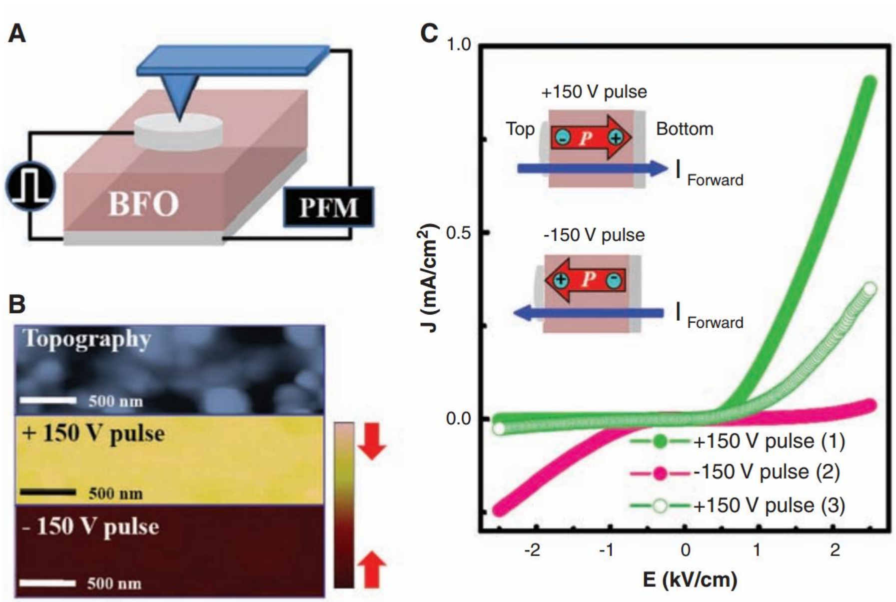


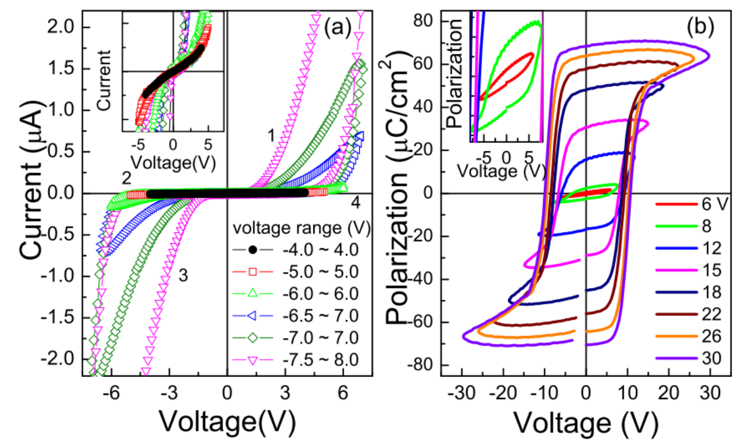
a reduced depletion-layer width, LRS

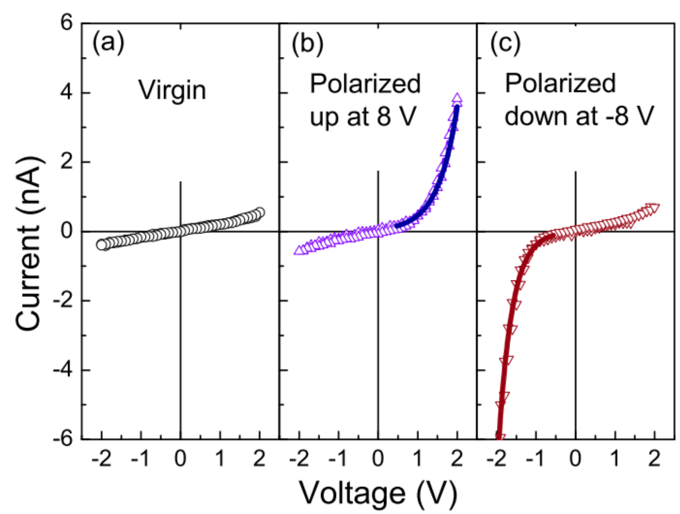
an enhanced depletion layer width, HRS

The mechanism of RS behavior in ferroelectric heterostructures

Polarization-dominated mechanisms







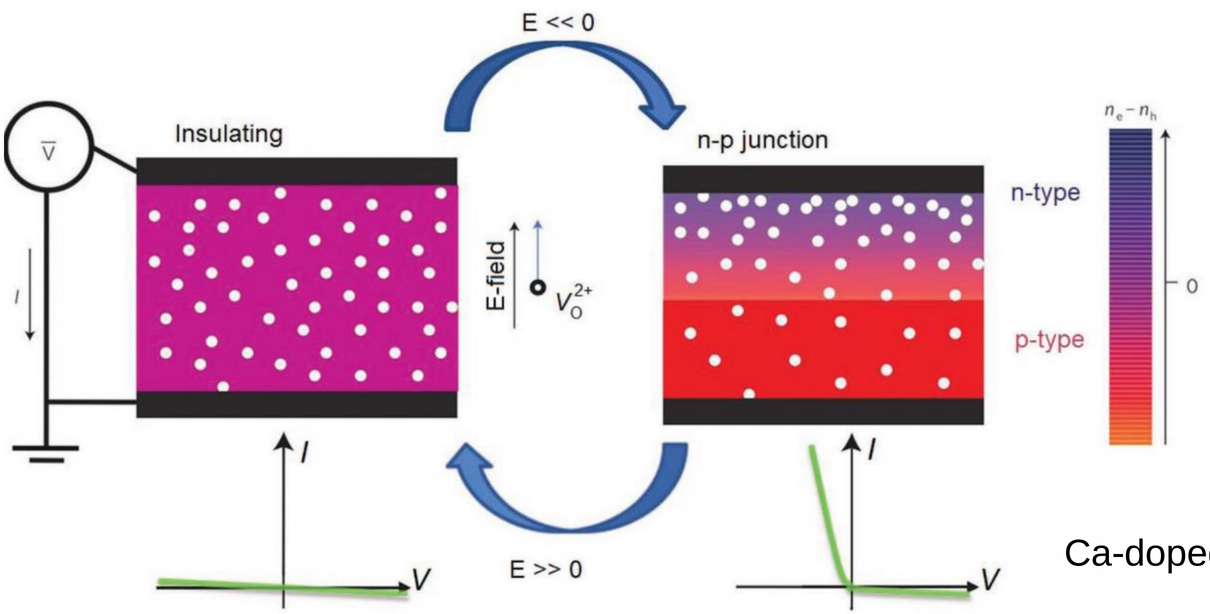
- ❑ interfacial resistance can be easily tuned because ferroelectric polarization has superior stability and inherent rapidity.

T. Choi et al. Science 2009, 324, 63.
C. Wang et al. Appl. Phys. Lett. 2011, 98, 192901.

The mechanism of RS behavior in ferroelectric heterostructures

2) a defect-dominated conduction mechanism

- When a negative voltage is applied to the heterostructures, oxygen vacancies can move and accumulate near one of the electrodes.
- As a result, the acceptor calcium ions cannot be balanced effectively by oxygen vacancies, **leading to an enrichment region of oxygen vacancies (n-type semiconductor) and an enrichment region of calcium ions (p-type semiconductor). The p–n junction is frozen, even if the negative voltage is turned off.**



Ca-doped $BiFeO_3$ on SRO

Figure 3. The RS mechanism with oxygen vacancy migration. The highly insulating state is thermodynamically stable (HRS). The oxygen vacancies respond to the electric field because the oxygen vacancies are positively charged as a consequence of their ionization. The oxygen vacancies move and accumulate near the interface with an electric field, forming a conductor (LRS). The value of $n_e - n_h$ represents the difference between the number of electrons and holes (the red color indicates that the number of holes is greater than that of electrons and vice versa). Reproduced with permission.[18b] Copyright 2009, Springer Nature.

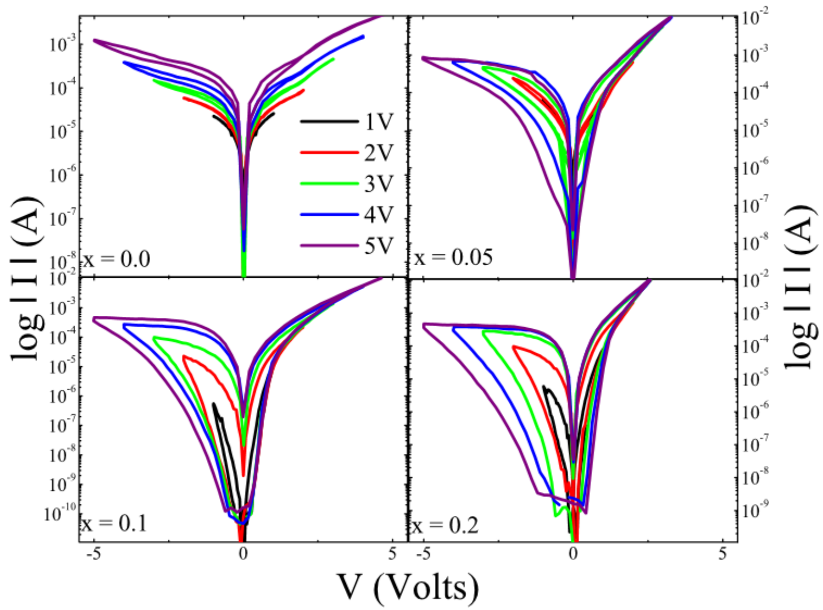
Approaches to Improve RS Properties

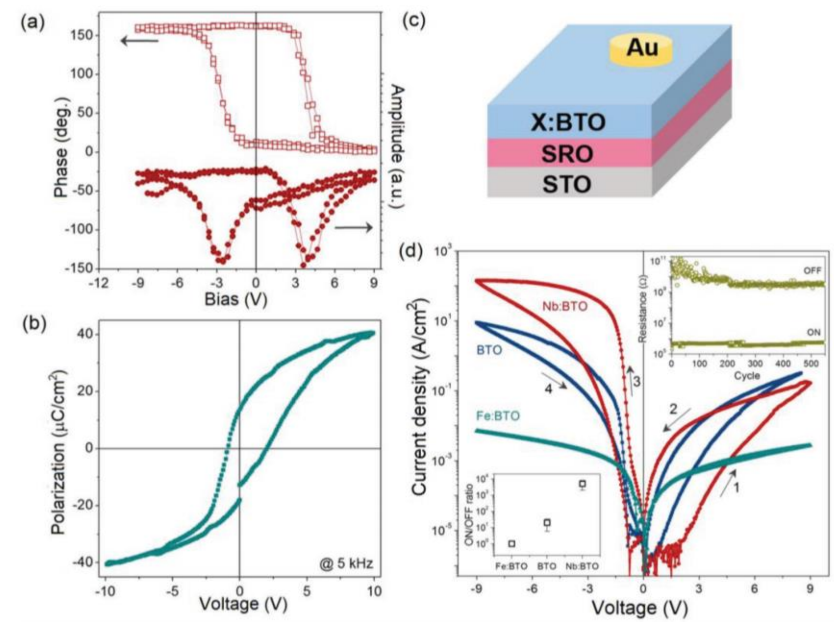
Typical Approaches

- Doping elements into the ferroelectric layer
- Controlling the oxygen vacancy concentration in the ferroelectric layer
- Optimizing the thickness of the ferroelectric layer or the electrode layer
- Constructing an insertion layer between the ferroelectric layer and the substrate

Approaches to Improve RS Properties

1. Doping elements into the ferroelectric layer





Ba-doped $BiFeO_3$ films on Nb:STO

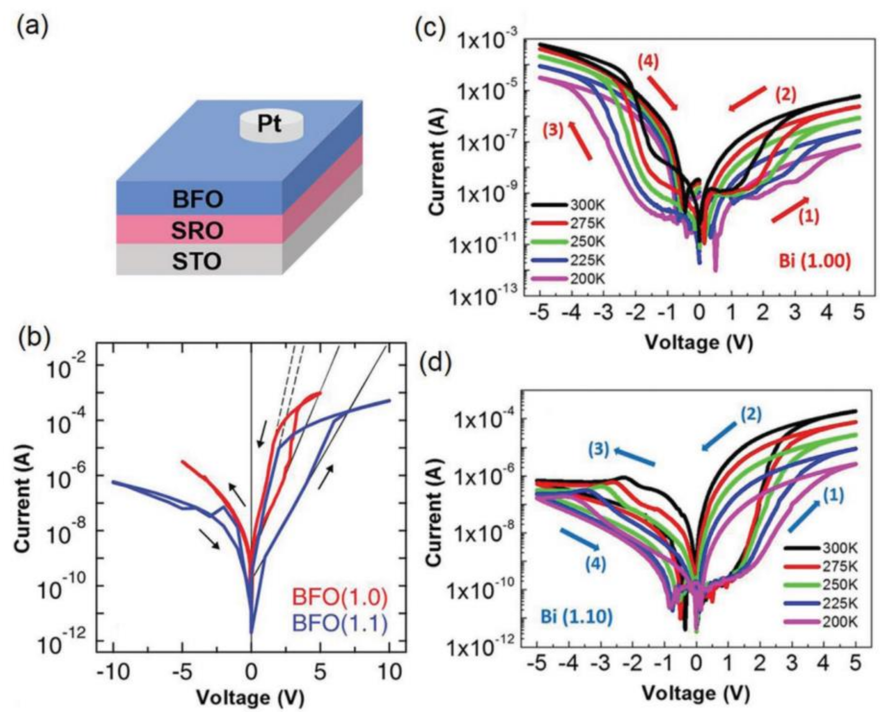
- ❑ The increase in ON/OFF ratio could be attributed to the increase of the oxygen vacancies.
- ❑ This provides **more conducting channels and promoting the modulation of the interfacial energy band**, corresponding to an LRS.

- ❑ Nb^{5+} donors simultaneously **improve the bulk limited current for the LRS** and **the interface-limited Schottky emission** for the HRS.
- ❑ However, Fe:BTO/SRO heterostructures always require bulk-limited insulators because Fe^{3+} acceptors dramatically **reduce the concentration of free electrons**, leading to a dramatic weakening of the modulation effect of the interface barrier.
- ❑ These results reveal the competitive relationship between ferroelectricity and conductivity in the RS behavior of ferroelectric heterostructures.

Approaches to Improve RS Properties

2. Controlling the oxygen vacancy concentration in the ferroelectric layer

- ❑ Control the oxygen pressure in the film deposition process and the ratio of raw materials.
- ❑ As a rule, higher oxygen pressure in the film deposition process leads to a lower oxygen vacancy concentration and better ferroelectricity in the ferroelectric films.



- ❑ The effect of the volatile element ratio in raw materials on RS behavior is more complex.
- ❑ The ON/OFF ratio decreased from 10^3 to 10 when the concentration of Bi exceeded 10% suggesting that Bi deficiency plays a crucial role in enhancing the ON/OFF ratio.

Appl. Phys. Lett. 2016, 108, 112902.

Approaches to Improve RS Properties

3. Optimizing the thickness of the ferroelectric layer or the electrode layer

---- balancing ferroelectric and conductive properties of ferroelectric heterostructure

- ❑ The scope of the interface effect is within a certain range in ferroelectric heterostructures, so the thickness of the ferroelectric layer or electrode layer is a key factor in determining the strength of the interface effect.
- ❑ The thickness of ferroelectric films have a effect on the domain distribution by strain relaxation, thicker films with less domain wall.

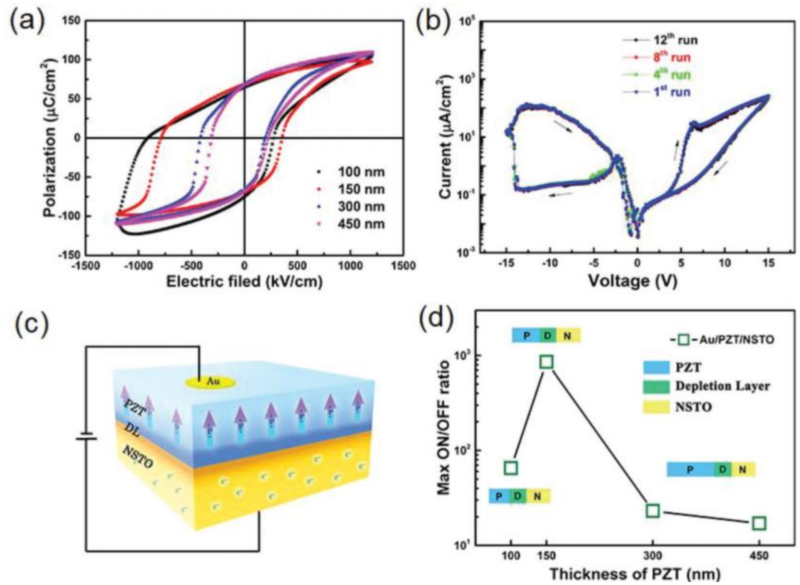


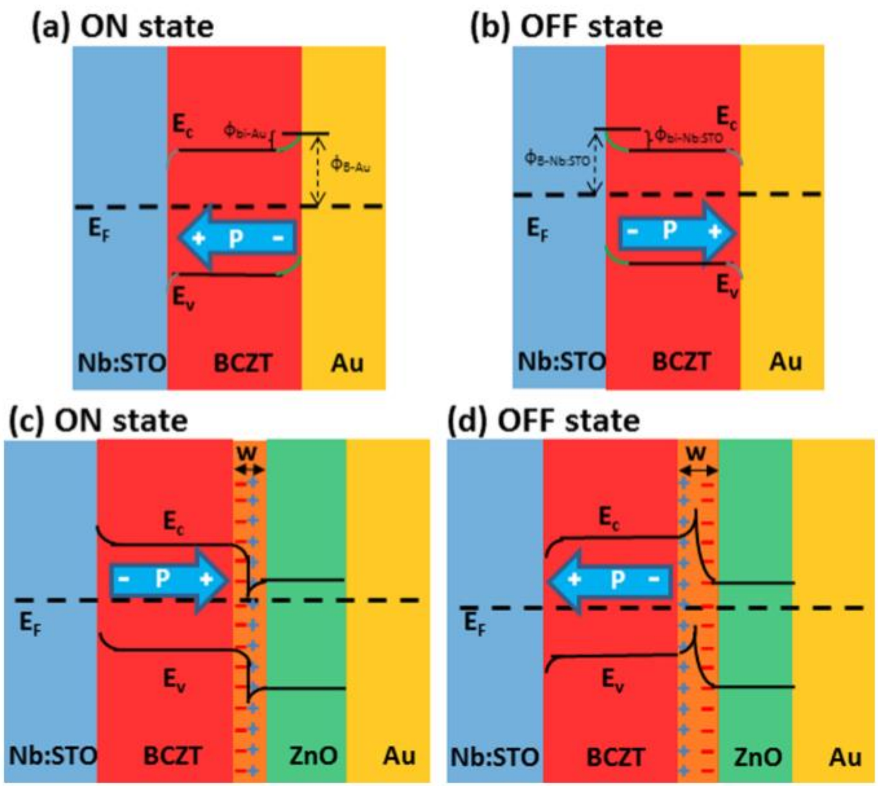
Figure 6. RS performance with the thickness of the ferroelectric layer. a) Polarization–electric field characteristics of the $Pb(Zr_{0.4}Ti_{0.6})O_3$/Nb:$SrTiO_3$ heterostructures with different thicknesses of $Pb(Zr_{0.4}Ti_{0.6})O_3$ films. b) Current–voltage curves for the $Pb(Zr_{0.4}Ti_{0.6})O_3$(150 nm)/Nb:$SrTiO_3$ heterostructures. c) Schematic of the device structure in this reference. d) ON/OFF ratios as a function of the $Pb(Zr_{0.4}Ti_{0.6})O_3$ thickness. All panels reproduced with permission.[24] Copyright 2016, American Chemical Society.

- ❑ The results indicate that the depletion layer at the **PZT/NSTO interface can be modulated** strongly by ferroelectric polarization but is **independent of the thickness of the PZT thin films**.
- ❑ The optimal thickness of the ferroelectric layer is determined by the width of the initial depletion layer, which is related to the **carrier concentration of the ferroelectric layer** and **the semiconductor electrode**, regardless of the ferroelectric polarization.

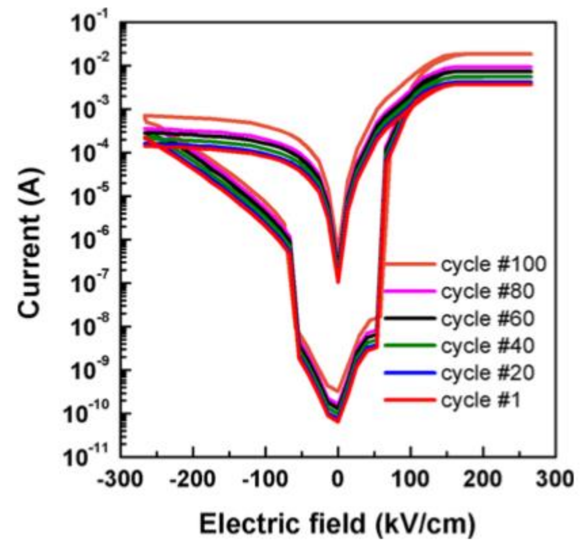
ACS Appl. Mater. Interfaces 2016, 8, 32948.

Approaches to Improve RS Properties

4. **Constructing an insertion layer between the ferroelectric layer and the substrate**



$0.5Ba(Zr_{0.2}Ti_{0.8})O_3{-}0.5(Ba_{0.7}Ca_{0.3})TiO/ZnO$

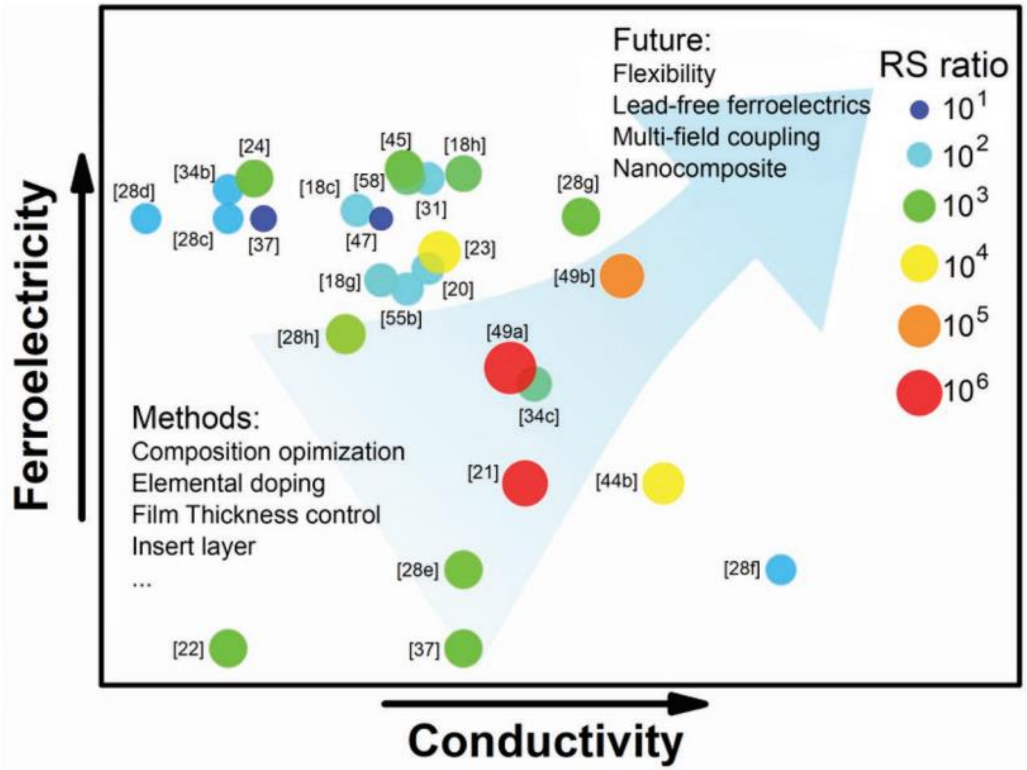


- The 15 nm thick ZnO film can provide an additional depletion layer with a thickness of 12 nm.
- The **larger the width of the depletion layer**, which can be modulated by ferroelectric polarization, the **more obvious the RS performance** is.

ACS Appl. Mater. Interfaces 2018, 10, 15240−15249

Summary

- ❑It is clear that ferroelectric heterostructures with both good ferroelectricity and conductivity exhibit excellent RS performance.
- ❑it is necessary to increase the conductivity of ferroelectric materials locally without significantly reducing the ferroelectricity.



Thanks for your attention