Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Diverse Polarization Bi-stability in Ferroelectric Tunnel Junctions due to the Effects of Electrode and Strain: An *ab initio* Study

G. L. Jiang,[ab] W. J. Chen,[abc]* Biao Wang,[c] Jian Shao[ab] and Yue Zheng[ab]*

[a]*State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics, Sun Yat-sen University, Guangzhou 510275, China. E-mail: zhengy35@mail.sysu.edu.cn.*

[b]*Micro&Nano Physics and Mechanics Research Laboratory, School of Physics, Sun Yat-sen University, Guangzhou 510275, China.*

[c]*Sino-French Institute of Nuclear Engineering and Technology, Sun Yat-sen University, Zhuhai, 519082, China. E-mail: chenweijin@mail.sysu.edu.cn.*

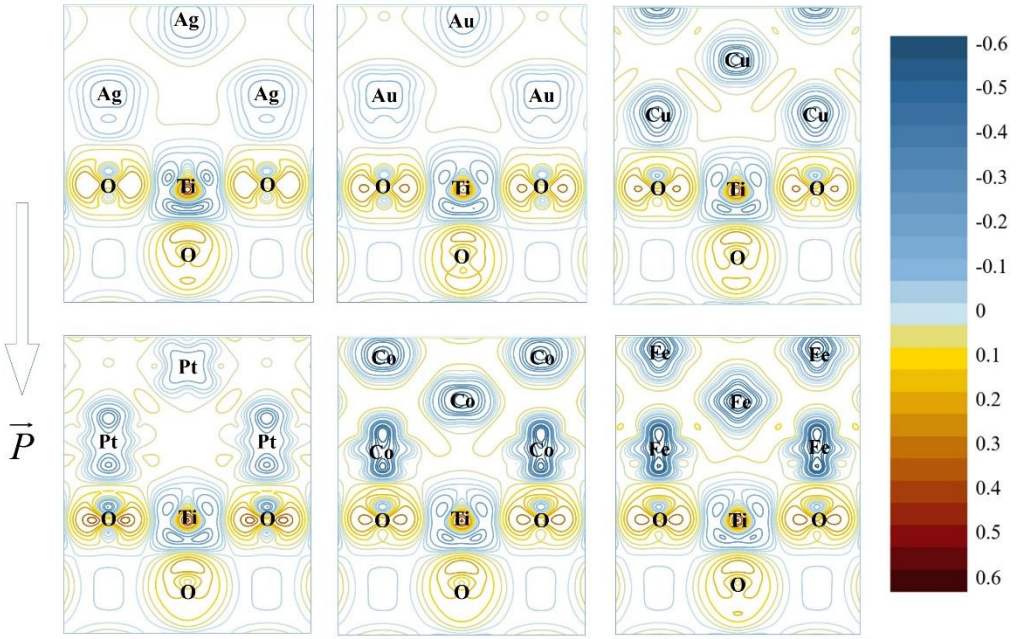

Figure S1. $\Delta\rho_{\text{scf-nscf}}$ distributions at M/TiO_2 interfaces with negative polarization which pointing to the BTO.

For comparison, we calculated the situations with negative polarization (pointing to the BTO film). Due to the lack of negative states at this thickness in A-FTJs, we choose to depict the $\Delta\rho_{\text{scf-nscf}}$ distributions of S-FTJs for alternative. Since the results are similar when the polarization is pointing to metal electrodes. It can be speculated that the direction of polarization have little influence on the charge density at M/TiO_2 interfaces.

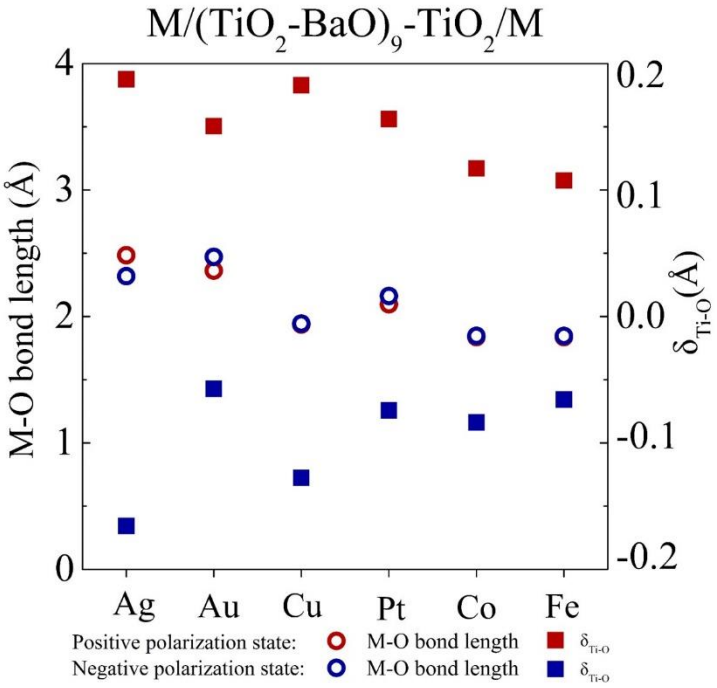

Figure S2. Computed structural parameters at the M/TiO_2 interfaces.

This trend is more intuitional when analyzing the interfacial structure. A series of computed structural parameters at the M/FTF interfaces of M/(TiO_2-BaO)$_9$/SRO junctions under -3% strain are depicted in Fig.S2. The square and cycle symbols represent the M-O bond length and Ti-O rumpling at the interface, respectively. Due to the absence of negative polarization of Ag/(TiO_2-BaO)$_9$/SRO and Cu/(TiO_2-BaO)$_9$/SRO, we choose to relax all structures with positive initial polarization for direct comparison. The positive Ti-O rumpling in the interfacial unit cell of Ag/(TiO_2-BaO)$_9$/SRO, Au/(TiO_2-BaO)$_9$/SRO and Cu/(TiO_2-BaO)$_9$/SRO is about 0.204Å, 0.164Å and 0.197Å, respectively. When we alter the top electrode to Pt, Co and Fe, this parameter changes to 0.077Å, 0.119Å and 0.116Å, respectively, which is generally

0.1Å smaller than that of Ag, Au and Cu junctions. To some degree, such results imply an enhancement of positive ferroelectric polarization when choosing M_w electrode. On the other hand, the M_s electrode may better stabilize the negative polarization state. It is noted that in spite of the shorter Cu-O bond length among its class, Cu/BTO interface still presents a quite large Ti-O rumpling, suggesting a more important role of bond strength than bond length in effecting the polarization bi-stability.

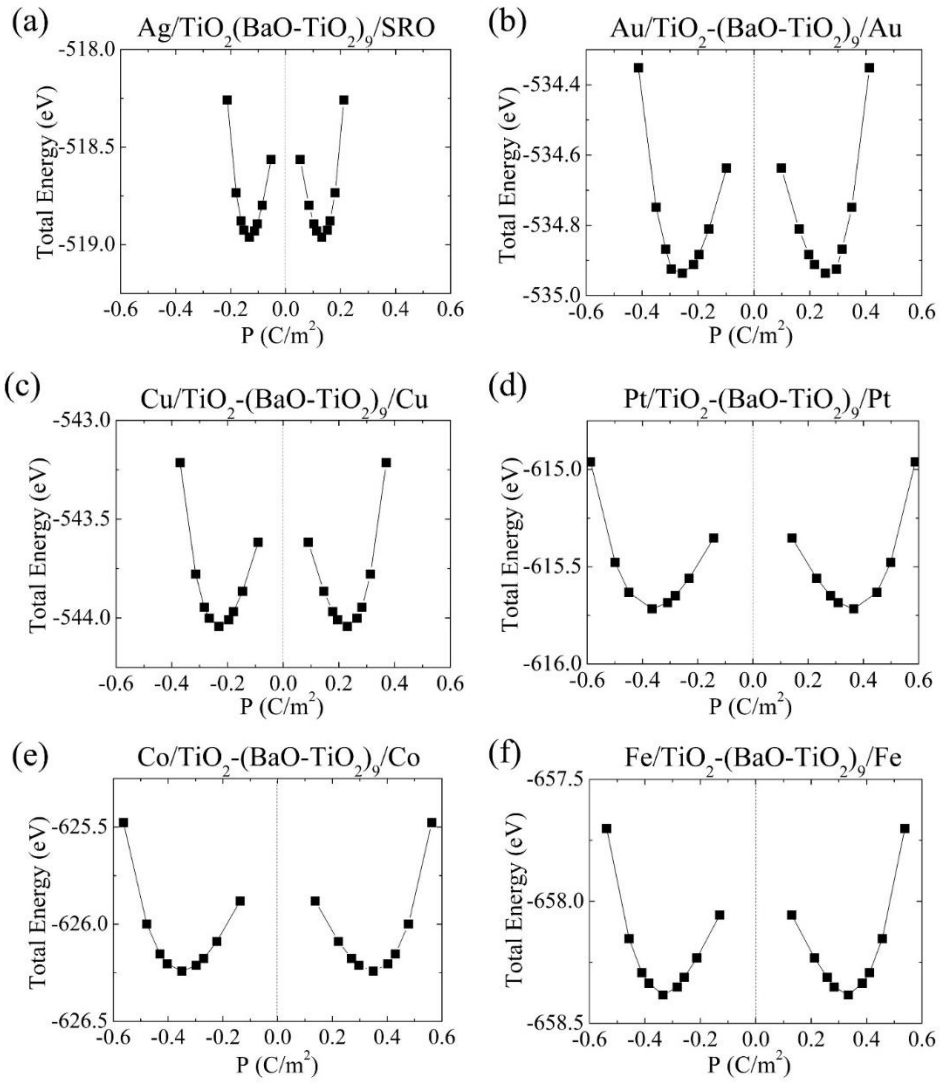

Figure S3. Double well total energy profile of the M/TiO_2-(BaO-TiO_2)$_9$/M symmetric junctions under -3% strain.

We calculate the double well profile for the symmetric structures with m = 9 unit cells of BTO. Without the difference between work functions of the two interfaces, the double well profile is supposed to be symmetrical with two polarization directions. It is worth noting that the minimal-energy polarization of M_w/(TiO_2-BaO)$_9$-TiO_2/M_w is small, especially the 0.132 C/m^2 of Ag/(TiO_2-BaO)$_9$-TiO_2/Ag, which is less than half

of the value of $M_s/(TiO_2\text{-}BaO)_9\text{-}TiO_2/M_s$ junctions. Such results could make sense because in $M_w/(TiO_2\text{-}BaO)_9\text{-}TiO_2/M_w$ junctions, the polarization directions are opposite at the two interfaces (see Fig.14 (a)-(c)), leading to a small average polarization in the whole junction.

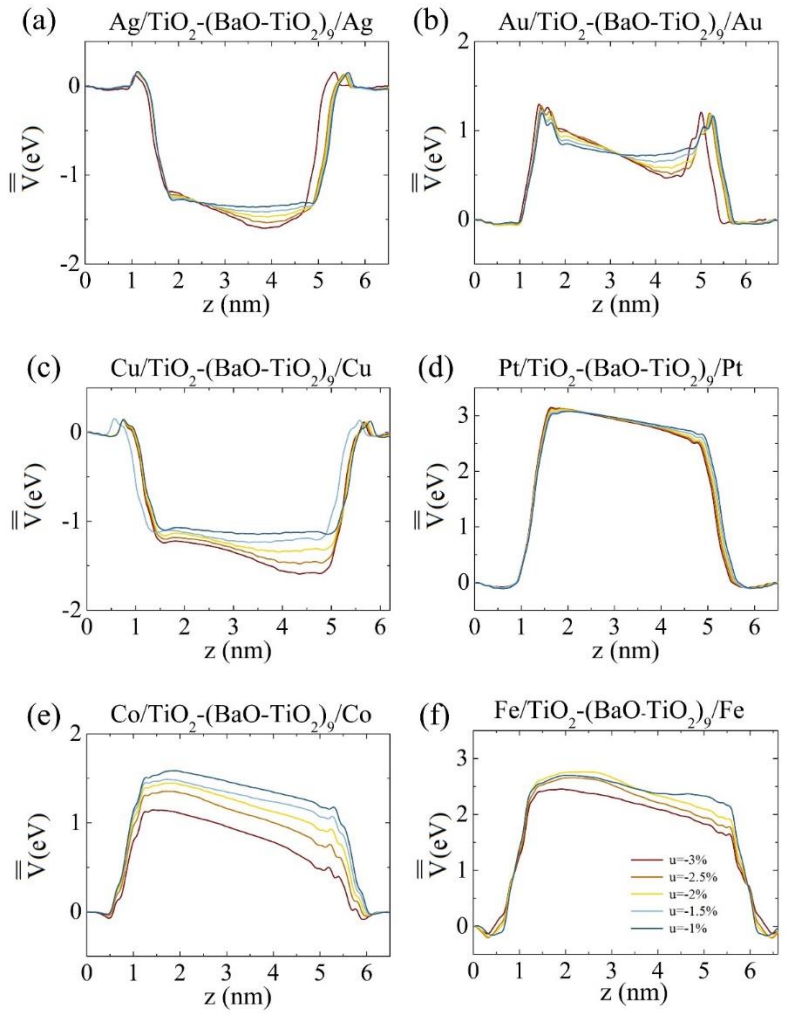

Figure S4. The strain-dependent macroscopic-averaged electrostatic potential energy profile along *z* direction $\overline{\overline{V}}(z)$ for M/TiO_2-(BaO-TiO_2)$_9$/M symmetric junctions. The strain ranges from -3% to -1%.

With the compressive strain decreasing from -3% to -1%, the depolarizing field in M_w/(TiO_2-BaO)$_9$-TiO_2/M_w tunnel junctions shrinks remarkably. When -1% strain is applied, the negative polarization in these three junctions is even completely neutralized, forming a kind of paraelectric state.

	Ag	Au	Cu	Pt	Co	Fe
$d_{Ru\text{-}O'}$(Å)	2.09	2.10	2.10	2.07	2.08	2.08
$d_{Ba\text{-}O'}$ (Å)	0.13	0.13	0.13	0.12	0.12	0.13
$d_{Ru\text{-}O''}$ (Å)	-0.01	-0.02	-0.01	-0.05	-0.04	-0.05

Table S1. The interfacial information of BaO/RuO_2 at electrode SRO in $M/(TiO_2\text{-}BaO)_9/SRO$ with positive initial polarization and -3% strain is listed. The differences (about 0.1Å) of the BaO/RuO_2 interfaces among different tunnel junctions are subtle. O’ and O’’ denote the oxygen atom in BaO and RuO_2, respectively.