A Solar Transistor and Photoferroelectric Memory

Amador Pérez-Tomás,* Anderson Lima, Quentin Billon, Ian Shirley, Gustau Catalan,* and Mónica Lira-Cantú*

This study presents a new self-powered electronic transistor concept “the solar transistor.” The transistor effect is enabled by the functional integration of a ferroelectric-oxide thin film and an organic bulk heterojunction. The organic heterojunction efficiently harvests photon energy and splits photogenerated excitons into free electron and holes, and the ferroelectric film acts as a switchable electron transport layer with tuneable conduction band offsets that depend on its polarization state. This results in the device photoconductivity modulation. All this (i.e., carrier extraction and poling) is achieved with only two sandwiched electrodes and therefore, with the role of the gating electrode being taken by light. The two-terminal solar-powered phototransistor (or solaristor) thus has the added advantages of a compact photodiode architecture in addition to the nonvolatile functionality of a ferroelectric memory that is written by voltage and nondestructively read by light.

1. Introduction

Transistors switch a semiconductor conductive state (or on-state) and an insulator state (or off-state) by means of a third additional terminal known as gate.[1–3] An external bias between their two flow electrodes is required for channel carriers to move, and this bias represents an undesirable yet unavoidable energy consumption. Harvesting the photon energy, a photovoltaic junction would already act as a self-powered current source, but incipient photovoltaic switches do not have a stable low energy consumption state.[4–10] Here, we report a new photoferroelectric transistor device concept based on a ferroelectric oxide/organic semiconductor heterojunction, where the ferroelectric acts as a reversibly polarizable electron transport media for the organic heterojunction photogenerated carriers. The resulting device is a two terminal (i.e., gate-less), low-cost (solution-processed), self-powered (solar illumination) nonvolatile phototransistor that switches between stable on and off states with a low energy consumption in the off state.

A phototransistor, photoswitch, or photo-field-effect transistor (FET)[11–13] can be defined as a three-terminal device whose output can be simultaneously and independently controlled by light or voltage.[14] Ideally, the phototransistor concept should be integrated into a vertical (sandwich-like) two-terminal device for larger density of miniaturization[15] while keeping a normally off state for better dissipation efficiency and easier control.[16] A reliable, cleanroom-less, low cost two-terminal phototransistor would represent a paradigm shift for the next generation of sustainable embodiments such as photodetectors, smart windows, flexible detector systems, and optical memories.[17] Nevertheless, such a device is unconventional and challenging since a photovoltaic semiconductor Schottky or p–n junction does not switch as internal fields and chemical potentials are not bistable.[16] There are however several photoswitchable mechanisms that can result in diverse types of photovoltaic responses; these include ferroelectric photovoltaics,[4–6] light-induced ionic drift in halide perovskites,[7,8] photovoltaic resistive switching,[9] and the photochromic effect.[10]

Among the photovoltaic materials enabling switching responses, ferroelectrics possess useful features in their switchable properties (a changeable direction of current and voltage by polarization switching) and in their anomalous photovoltaic effect that can generate photovoltages much bigger than the bandgap.[18,19] Nevertheless, their inherently low photocurrents (in the range of nA–µA cm−2) have resulted in poor overall photovoltaic efficiency.[19,20] A way to improve the photovoltaic current of ferroelectric solar cells is through the combination with organic[21–25] or inorganic light absorbers.[26–32]

It has been theoretically[33] and experimentally demonstrated[34–36] that ferroelectrics bend their electronic band structure and offsets with respect to adjacent metals and metal-oxides when switching the ferroelectric polarization. As illustrated in Figure 1a, it is the objective of this study to implement this unique feature to design a new class of compact two-terminal photovoltaic transistors. Here, we demonstrate an efficient (normally off) gate-less (two-electrode) phototransistor where the conductivity modulation is achieved by the polarization state of a ferroelectric oxide interlayer while the efficient light harvesting channel region is a bulk organic heterojunction. The normally off operation is a key and unreported device enabling feature so far, and the canonical bulk photovoltaic effect currents switch between positive and negative values and no in between on and off conductivity states.

Dr. A. Pérez-Tomás, A. Lima, Q. Billon, I. Shirley, Prof. G. Catalan, Prof. M. Lira-Cantú
Catalan Institute of Nanoscience and Nanotechnology (ICN2)
CSIC and The Barcelona Institute of Science and Technology
Campus UAB, Bellaterra, 08193 Barcelona, Spain
E-mail: amador.perez@icn2.cat; gustau.catalan@icn2.cat; monica.lira@icn2.cat
Prof. G. Catalan
Institut Català de Recerca i Estudis Avançats (ICREA)
08010 Barcelona, Catalonia

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201707099.

DOI: 10.1002/adfm.201707099
2. The Solar Cell

In the proposed configuration, the wide bandgap ferroelectric layer acts as both the transparent electron transport material and as a switchable interface, as shown in Figure 1b. Efficient light harvesters based on organic semiconductors are defined on top the ferroelectric. Organic semiconductors are cheap, flexible, lightweight, made with abundant materials and have low environmental impact.\(^{[37]}\) Usefully, they are synthesized at lower temperatures than oxides, so they can be grown on top of the ferroelectric layer without causing damage. As an additional advantage, the organic semiconductor absorbs light in the solar visible range, thus circumventing one of the key difficulties of working with photoferroelectrics, which is that...
their normally wide bandgap confines their optimum performance to the ultraviolet spectrum.\(^9\)

An organic bulk heterojunction is made of an electron donor (e.g., rr-poly(3-hexylthiophene-2,5-diy) (P3HT) polymer) and an electron acceptor (e.g., [6,6]-Phenyl-C61-butyric acid methyl ester (PCBM) fullerene) organic compounds; the p-type “donor” absorbs a photon while the n-type “acceptor” acquires an electron (Figure 1b). An efficient heterojunction network allows the donor polymer to contact a hole transport medium (HTM) and the acceptor fullerene to contact an electron transport medium (ETM), facilitating the extraction of charge without recombination. The transport medium may be an oxide thin film that (i) tunes the Schottky barrier alignment and (ii) selects the majority carriers to avoid recombination.\(^1\) The HTM must establish an anode ohmic contact and select holes. For this purpose, we select a thin layer of V₂O₅.\(^3\) Meanwhile, for the ETM we chose thin films of the archetypical ferroelectric Pb(Zr,Ti)O₃ (x = 0.53) layer, hereafter labeled as PZT, coated on the glass/fluorine tin oxide (FTO) substrate (see the Experimental Section). Although ferroelectric PZT is often treated as an insulator, it is in fact an n-type wide-bandgap semiconductor\(^4\) so it is apt as an ETM. In addition, having switchable polarization means that its interfacial band bending and thus its contact resistivity can be tuned. This adds a new degree of freedom to the functionality of the device; specifically, the nonvolatile nature of the polarization means that the photogated transistor can also act as a memory device.

The energy band structure of the ferroelectric is shown in Figure 2 as determined by ultraviolet photoelectron spectroscopy (UPS) and ultraviolet–visible spectrophotometry (UV–Vis) (see the Experimental Section; Figures S1–S3, Supporting Information). The ferroelectric PZT perovskite phase was evidenced by an X-ray powder diffraction (XRD) scan for annealing temperatures higher than 600 °C with a preferential orientation in <110> (see Figure S4 in the Supporting Information). The ferroelectric layer exhibited excellent ferroelectric characteristics as shown by the typical ferroelectric hysteresis polarization–voltage curve as shown in Figure 2c for an undiluted PZT layer (=90 nm-thick) defined at 625 °C. The optimal PZT anneal temperature has been determined to be 625 °C and all the poling experiments described below have been carried out with the ferroelectric electron transport layer defined at this temperature. The remnant polarization at the ferroelectric surfaces is larger than 20 μC cm⁻². The standard size of the capacitor for the hysteresis loops characterization was circular dots geometry with 200 μm in diameter (3.14 × 10⁻⁴ cm²).

Because of the wide bandgap of the transparent conducting oxide (FTO) and the ferroelectric electron transport media, the great majority of the photons are able to reach the organic light-absorbing heterojunction. The photogenerated electrons and holes are then selectively collected by the electron and hole transport materials, (PZT and V₂O₅ respectively), which also act as barriers for minority carriers (Figures S5 and S6, Supporting Information). The photogenerated electrons and holes are thus extracted from the core device at their respective metallic electrodes which band alignments and offsets have also been determined by UPS and UV–Vis spectroscopy, as shown in Figure 2d. The photovoltaic performances (in particular, the photovoltaic current density) of the proposed device have been optimized by varying the PZT layer thickness and its anneal temperature, as shown in Figure 3.

The conductivity of the bare ferroelectric layer is extremely small. At room temperature, PZT is a good dielectric insulator with a conductivity of less than 10⁻¹² Ω⁻¹ cm⁻¹. The bandgap of the PZT lies in the ultraviolet (=3.6 eV), making the PZT layer poorly absorbing in the visible part of the spectrum (see Figure S1 in the Supporting Information). The ferroelectric photovoltaic properties of the FTO/PZT/Ag structure were tested under AM1.5G irradiation conditions (see Figure S7 in the Supporting Information). The area of the devices was 0.18–0.20 cm², larger than usual for vertical photoferroelectric capacitors, which are typically microscale.\(^5\) In optimal conditions, only a very weak photovoltaic current of \(j_{sc} = (3 ± 2) \times 10^{-3}\) mA cm⁻² was observed for simple photoferroelectric capacitors, similar to previous state-of-the-art large-area ferroelectric devices.\(^6\)

3. The Solar Transistor (Solaristor)

The ferroelectric polarization introduces nonvolatile transistor-effect functionality into the photovoltaic junction as shown in Figure 2e.f. In the following, the poling electrode is the top silver layer, while the bottom FTO is always grounded. Switching the polarization up or down changes the electron transport material conduction band offset and thus modulates the ferroelectric/organic semiconductor contact resistance from a state of high resistance (or off) to a state of low resistance (or on). A ferroelectric downward poling (positive bias) results in a shift of the ferroelectric valence band toward deeper energies. Accordingly, the conduction band offset (\(\Delta E_c\)) between the fullerene PCBM lowest unoccupied molecular orbital (LUMO n-type) and the PZT conduction band decreases. The lower energy barrier results in a higher electron current. Conversely, a ferroelectric upward poling (negative bias) reduces the ionization potential of valence band electrons and \(\Delta E_c\) increases, and the high energy barrier results in reduced photocurrent. Meanwhile, neither downward polarization nor upward polarization\(^4\) permits hole transport because PZT is n-type. The high resistivity of the electron transport material barrier layer blocks residual leakage current and sustains the off-state.

The performance of one of our large area (0.2 cm²) photovoltaic transistor devices is illustrated in Figure 4. The standard poling process for this experiment is a DC bias applied to the silver terminal. The duration of the DC pulse was few seconds. A ±20 V DC bias pulse is enough to switch on/off the photovoltaic transistor for the thicker PZT, while the thinnest could be switched with ±5 V. A positive poling results in negative \(\Delta E_c\) and no ferroelectric/organic semiconductor interface barrier, enabling photocurrents of 5–10 mA cm⁻². In contrast, applying
a negative voltage switches the polarization upward, thus raising the blocking barrier. This results in a drop of the photocurrent, which is only 0.01 mA cm\(^{-2}\), a three order of magnitude difference with respect to the on-state. This off state can be reversed back applying positive bias to the anode again (DC bias +20 V/10 s). The phototransistor behavior is consistent after subsequent poling cycles (see Figure 4c) and photocurrents are retained over time (Figure S10, Supporting Information). It must be also mentioned that, consistent with the band alignment explanation, the conductivity differences upon the polarization state of the ferroelectric layer are preserved in the dark (Figure 4b), resulting in a resistive switching device.\(^{[15]}\)

We foresee several routes to improve the device performance. On one hand, the solar transistor power conversion efficiency may be further improved by using alternative and more efficient light absorbers such as halide perovskites. On the other
hand, ferroelectric oxide thin films can also deliver improved performances in distinct ways. Ferroelectric thin films with more pronounced band offsets, for example, can in principle improve the on/off ratio of the device as well as the transistor’s photocurrent and power conversion efficiency. In addition, narrower bandgap ferroelectrics such as BiFeO₃ or BiCrFeO₃ can theoretically contribute to the light harvesting; such visible bandgap ferroelectric oxides could act as the light absorber itself in an all-oxide solution. Alternatively, ferroelectric oxides with even wider bandgaps than PZT (i.e., more solar blind) would allow all the solar radiation to pass through the electron transport layer reaching the active layers without attenuation. In any case, we think that this work opens new and exciting possibilities within the frontier of ferroelectrics, photonics, electronics, and photovoltaics.

The main lesson from this investigation is that ferroelectrics can be exploited not just as photovoltaic materials in their own right, but also as (switchable) charge transport layers photovoltaic devices. In this context, ferroelectric oxides add new functionalities to the structure; in the present case, a two-electrode self-powered phototransistor has been demonstrated. Under sunlight illumination, the absorbing organic bulk heterojunction acts as a self-powered source of photogenerated electron and holes that are driven toward their respective electrodes. Conventional photodiodes do not switch, but here, the modification of the electron transport layer barrier offsets due to the stable gating effect of the ferroelectric polarization, which enables the on–off switching of the photodiode. As an additional advantage, the conventional phototransistor’s footprint and interconnection complexity are greatly reduced by moving from the standard in-plane three-electrode architecture to a vertical, two-electrode photodiode-like architecture.

While the new device concept is described as a phototransistor, its design is multifunctional and may be used for other photonic applications. For example, the device is also a photonic ferroelectric random-access memory where the bits are written via an electrical pulse, but read nondestructively using a light pulse that excites a high current in the on state, but low current in the off state.

4. Conclusions

In conclusion, a transistor effect has been evidenced by combining organic P3HT:PCBM-based solar cells with a ferroelectric layer acting as switchable electron transport medium. Here, we demonstrate that a photocurrent variation of various orders of magnitude can be obtained by varying the ferroelectric polarization of the PZT layer and the band alignment in the device. This finding expands the switching capabilities of previous devices combining ferroelectric layers with photovoltaic devices, demonstrating a conductivity that can be switched by voltage and gated by light. Therefore, the solar transistor (or solaristor) opens new device possibilities both as light-powered logic device and as photointerrogated memory device.

5. Experimental Section

Materials: The synthesis of the PZT solution was done as follows: Zr-isopropoxide (Zr[OCH(CH₃)₂]₄ (70 wt%) in 1-propanol, Sigma) and Ti-isopropoxide (Ti[OCH(CH₃)₂]₄ (97%), Sigma) were mixed and then diluted in acetic acid and n-propanol; 5 mL acetic acid and 10 mL of
n-propanol were added to the Zr/Ti solution. Afterward, Pb acetate (10% excess) [lead(II) acetate trihydrate, Pb(CH₃CO₂)₂ · 3H₂O (99.999%) Sigma] was dissolved into the above solution by heating the solution in a silicon oil bath at 85 °C for dissolving the Pb precursor completely. After cooling down the solution to room temperature, acetic acid and distilled water were added to modify the Pb–Zr–Ti solution and to adjust the 40 mL solution to 0.4 m. The active polymer:fullerene layer was formed by mixing 98% P3HT from Merk and PCBM (99.5%) from Solenne. To prepare the organic bulk heterojunction, 15 mg of each component was mixed with 0.5 mL of dichlorobenzene. Synthesis of the V₂O₅–H₂O xerogel was carried out by the cationic exchange method. Briefly, 4.5 g of sodium metavanadate (NaVO₃; Sigma) was dissolved in water at 80 °C. Once cold, the solution was passed through a cationic exchange DOWEX50 WX2 50–100 (Sigma). The initial colorless solution changed to yellow-orange corresponding to the formation of the metavanadic acid. The polycondensation of the vanadic acid resulted in the formation of the V₂O₅ gel (red) after 1 month standing at room ambient conditions. Finally, a layer of 100 nm of silver was evaporated on top of the V₂O₅ layer in a BOC EDWARDS AUTO 306 thermal hot plate. This final annealing was observed to significantly improve the photovoltaic current out from the structure.

Material and Device Characterization—XRD: XRD analyses between 5 and 120 degrees in a RIGAKU Rotaflex RU200 B instrument, using CuKα1 radiation.

Material and Device Characterization—X-ray Photoelectron Spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS): The XPS and UPS measurements were performed with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany) in ultra-high vacuum conditions (base pressure 3E-10 mbar). XPS measurements were performed with a monochromatic Kα X-ray source (1486.74 eV) and UPS measurements were realized with monochromatic HeI UV source (21.2 eV). Work function determination was done by applying bias of −10 V at the sample.

Device Fabrication: The FTO substrates were bought from Solems, model ASAHL 100 by chemical vapor deposition of 1.1 mm thickness (70–100 ohm resistance, thickness of FTO layer 800 Å) and were etched with a mixture of Zn powder (299%, Aldrich), and hydrochloric acid (HCl) (ACS reagent 37% from Sigma Aldrich). To define the cathode of the solar transistor, two-thirds of the FTO substrate was protected with a cellotape and then the zinc powder, with no further treatment, was carefully sprinkled in the unprotected part to cover the entire FTO surface. A diluted hydrochloric acid (0.2 µ) solution was then dropped by a pipette onto the FTO/Zn-powder region. The conductive FTO was further removed from the glass by mechanical exfoliation with a cotonnet and thus, a bare insulating glass region for the cathode pad deposition was defined. The etched substrates were then cleaned with soap water, mili-Q water and ethanol (99.5%), dried with N₂, and treated under UV– ozone treatment for 20 min before use.

Once cleaned, 80 µL of Pb–Zr–Ti solution was spin-coated with a precision autoclavable pipette on top of the central FTO region with the etched FTO/glass back of the chip vacuum-clamped onto the stopped spin-coating system. The active region was masked by Kapton tape. Immediately after the wetting, the Pb–Zr–Ti compact layer was defined at 4000 rpm with an acceleration of 2000 rpm s⁻¹ for 40 s. The solution was dried in the hot plate for 5 min at 150 °C. The Pb–Zr–Ti layer was further annealed (400–650 °C) for 10 min in air to form the functional oxide Pb(Zr,Ti)O₃ (or PZT). A single layer of PZT from undiluted 0.4 µ Pb–Zr–Ti solution was 90–100 nm thick. Depending on the final desired thickness of the ferroelectric oxide, this coating procedure could be repeated up to three times. Alternatively, the Pb–Zr–Ti solution was diluted in parts of acetic acid to define thinner ferroelectric electron transport oxides, as shown in the Supporting Information. The 0.4 µ Pb–Zr–Ti solution dilution in parts of acetic acid progressively reduced the thickness of the final PZT layer up to a value of <5 nm for 1:1.5 (i.e., 150 µL of 0.4 µ Pb–Zr–Ti solution diluted in 2.25 mL of acetic acid). The optimal PZT anneal temperature had been found to be 625 °C, which balanced the temperature required for the ferroelectric perovskite phase formation while keeping low the thermal budget for the FTO surface. The PZT layer was cooled-down to room temperature and then was ready for the next step. The PZT surface was not submitted to any polishing or additional cleaning step.

Afterward, the P3HT:PCBM solution (30 mg mL⁻¹ in chlorobenzene) was spin-coated on top of the ferroelectric oxide layer at 1000 rpm. Then, a solution of V₂O₅–H₂O xerogel (1:1) was spin-coated at 1000 rpm and annealed at 120 °C for 5–10 min in a hot plate under ambient conditions. Finally, a layer of 100 nm of silver was evaporated on top of the V₂O₅ layer in a BOC EDWARDS AUTO 306 thermal evaporator using shadow masks. After the electrodes metal deposition, a final thermal annealing was carried out at 120 °C for 10 min in air in the hot plate. This final annealing was observed to significantly improve the photovoltaic current out from the structure.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
A.P.T., M.L.C., and G.C. conceived the experiments. A.P.T. was in charge of the experimental and characterization work assisted by A.L., Q.B., and I.S. All authors analyzed the data and cowrote the paper. A.P.T. acknowledges Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional under contract ENE2015-74275-JIN. All authors acknowledge Prof. Martijn Kemerink (Linköping University) for their
valuable comments, Dr. G. Sauthier for the XPS/JUPS measurements, S. Amores for the lamella fabrication, and Dr. B. Ballesteros for the TEM inspection. The ICN2 is funded by the CERCA programme / Generalitat de Catalunya and by the Severo Ochoa programme of the Spanish Ministry of Economy, Industry and Competitiveness (MINECO, grant no. SEV-2013-0295), for the grant ENE2016-79282-C5-2-R and the OrgEnegy Excellence NetworkCTQ2016-81911-REDT. To the Agència de Gestió d’Ajuts Universitaris i de Recerca for the support to consolidated Catalonia research groups 2014SGR 1212 and 1216-F. To the COST Action StableNextSol project MP1307 and to the European Research Council (ERC) Starting Grant, project No. 308023.

**Conflict of Interest**
The authors declare no conflict of interest.

**Keywords**
electron transport layers, ferroelectric photovoltaics, nonvolatile memory, organic bulk heterojunctions, phototransistors

Received: December 6, 2017
Revised: January 7, 2018
Published online: February 28, 2018

[1] a) J. E. Lilienfeld, US1745175A 1925
b) J. E. Lilienfeld, US1900018 1928;
c) J. Bardeen, W. H. Brattain, US2524035A 1948;
d) W. Shockley, US2569347A 1948.

[2] I. Ferain, C. A. Colinge, J.-P. Colinge, Nature 2011, 479, 317.

[3] J. A. del Alamo, Nature 2011, 479, 317.

[4] H. Yi, T. Choi, S. Choi, Y. Oh, S. W. Cheong, Adv. Mater. 2011, 23, 3403.

[5] W. Ji, K. Yao, Y. C. Liang, Adv. Mater. 2010, 22, 1763.

[6] L. Zhang, J. Chen, J. Cao, D. He, X. Xing, J. Mater. Chem. C 2015, 3, 4706.

[7] Y. Yuan, J. Chae, Y. Shao, Q. Wang, Z. Xiao, A. Centrone, J. Huang, Adv. Energy Mater. 2015, 5, 1500615.

[8] Z. Xiao, Y. Yuan, Y. Shao, Q. Wang, D. Bi, P. Sharma, A. Gruverman, J. Huang, Nat. Mater. 2015, 14, 193.

[9] S. Nau, C. Wolf, S. Sax, E. J. W. List-Kratochvil, Adv. Mater. 2015, 27, 1048.

[10] M. El Gemayel, K. Börjesson, M. Herder, D. T. Duong, J. A. Hutchison, C. Ruzié, G. Schweicher, A. Salleo, Y. Geerts, S. Hecht, E. Orgiu, P. Samori, J. Mater. Chem. A 2015, 6, 6330.

[11] D. Kufer, G. Konstantatos, ACS Photonics 2016, 3, 2197.

[12] F. P. García de Arquer, A. Armin, P. Meredith, E. H. Sargent, Nat. Rev. Mater. 2017, 2, 16100.

[13] H. Wang, D. H. Kim, Chem. Soc. Rev. 2017, 46, 5204.

[14] K. Börjesson, M. Herder, L. Grubert, D. T. Duong, A. Salleo, S. Hecht, E. Orgiu, P. Samori, J. Mater. Chem. C 2015, 3, 4156.

[15] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, Nature 2008, 453, 80.

[16] S. M. Sze, K. K. Ng, Physics of Semiconductor Devices, John Wiley & Sons, Inc., Hoboken, NJ, USA 2006.

[17] Y. Wakayama, R. Hayakawa, H-S. Seo, Sci. Technol. Adv. Mater. 2014, 15, 024202.

[18] A. Pérez-Tomás, M. Lira-Cantú, G. Catalan, Adv. Mater. 2016, 28, 9644.

[19] P. J. Sturman, V. M. Fridkin, Photovoltaic and Photo-refractive Effects in Noncentrosymmetric Materials, Gordon and Breach Science Publishers, PA, USA 1992.

[20] J. E. Spanier, V. M. Fridkin, A. M. Rappe, A. R. Akbashev, A. Polemi, Y. Qi, Z. Gu, S. M. Young, C. J. Hawley, D. Imbrenda, G. Xiao, A. L. Bennett-Jackson, C. L. Johnson, Nat. Photonics 2016, 10, 611.

[21] Y. Yuan, T. J. Reece, P. Sharma, S. Poddar, S. Ducharme, A. Gruverman, Y. Yang, J. Huang, Nat. Mater. 2011, 10, 296.

[22] K. Asadi, P. de Bruyn, P. W. M. Blom, D. M. de Leeuw, Appl. Phys. Lett. 2011, 98, 183301.

[23] Y. Yuan, P. Sharma, Z. Xiao, S. Poddar, A. Gruverman, S. Ducharme, J. Huang, Energy Environ. Sci. 2012, 5, 8558.

[24] K. S. Nalwa, J. A. Carr, R. C. Mahadevapuram, H. K. Kodali, S. Bose, Y. Chen, J. W. Petrich, B. Ganapathyubramanian, S. Chaudhary, Energy Environ. Sci. 2012, 5, 7042.

[25] K. Shin, T. Y. Kim, G. C. Yoon, M. K. Gupta, S. K. Kim, W. Seung, H. Kim, S. Kim, S. M. Kim, S-W Kim, Adv. Mater. 2014, 26, 5619.

[26] D. Cao, C. Wang, F. Zheng, W. Dong, L. Fang, M. Shen, Nano Lett. 2012, 12, 2803.

[27] F. Zheng, Y. Xin, W. Huang, J. Zhang, X. Wang, M. Shen, W. Dong, L. Fang, Y. Bai, X. Shen, J. Hao, J. Mater. Chem. A 2014, 2, 1363.

[28] Z. Fan, K. Yao, J. Wang, Appl. Phys. Lett. 2014, 105, 162903.

[29] F. Wu, Y. Guo, Y. Zhang, H. Duan, H. Li, H. Liu, J. Phys. Chem. C 2014, 118, 15200.

[30] L. Loh, J. Briscoe, S. Dunn, Nanoscale 2014, 6, 7072.

[31] D. Tiwari, D. J. Fermin, T. K. Chaudhuri, A. J. Ray, J. Phys. Chem. C 2015, 119, 5872.

[32] P. Zhao, L. Bian, L. Wang, J. Xu, A. Chang, Appl. Phys. Lett. 2014, 105, 013901.

[33] M. Stengel, P. Aguado-Puente, N. A. Spaldin, J. Junquera, Phys. Rev. B 2011, 83, 235112.

[34] F. Chen, A. Klein, Phys. Rev. B 2012, 86, 094105.

[35] J. E. Rault, G. Aguerras, T. Maroutian, V. Pillard, P. Lecoeur, G. Niu, B. Vilquin, M. G. Silly, A. Bendounan, F. Sirotti, N. Barrett, Phys. Rev. B 2013, 87, 155146.

[36] F. Wong, G. Perez, M. Bonilla, J. A. Colon-Santana, X. Zhang, P. Sharma, A. Gruverman, P. A. Dowben, L. G. Rosa, RSC Adv. 2014, 4, 3020.

[37] O. Ostroverkhova, Chem. Rev. 2016, 116, 13279.

[38] A. Pérez-Tomás, A. Mingorance, D. Tenenbaum, M. Lira-Cantú, Metal Oxides in Photovoltaics: All-Oxide, Ferroic, and Perovskite Solar Cells (Ch. 8) in The Future of Semiconductor Oxides in Next-Generation Solar Cells, Elsevier, Amsterdam, Netherlands, p. 267, 2018.

[39] G. Terán-Escobar, J. Pampel, J. M. Caicedo, M. Lira-Cantú, Energy Environ. Sci. 2013, 6, 3088.

[40] J. F. Scott, Ferroelectric Memories, Springer-Verlag, Berlin, Heidelberg 2000.

[41] R. Nechache, C. Harnagea, S. Li, L. Cardenas, W. Huang, J. Chakrabarty, F. Rosei, Nat. Photonics 2014, 9, 61.

[42] F. Zheng, P. Zhang, X. Wang, W. Huang, J. Zhang, M. Shen, W. Dong, L. Fang, Y. Bai, X. Shen, H. Sun, J. Hao, Nanoscale 2014, 6, 2915.

[43] B. Chen, Z. Zuo, Y. Liu, Q.-F. Zhan, Y. Xie, H. Yang, G. Dai, Z. Li, G. Xu, R.-W. Li, Appl. Phys. Lett. 2012, 100, 173903.

[44] D. Tiwari, S. Dunn, J. Mater. Sci. 2009, 44, 5063.