Giant bulk photovoltaic effect in solar cell architectures with ultra-wide bandgap Ga$_2$O$_3$ transparent conducting electrodes

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**A B S T R A C T**

The use of ultra-wide bandgap transparent conducting beta gallium oxide (β-Ga$_2$O$_3$) thin films as electrodes in ferroelectric solar cells is reported. In a new material structure for energy applications, we report a solar cell structure (a light absorber sandwiched in between two electrodes - one of them - transparent) which is not constrained by the Shockley–Queisser limit for open-circuit voltage ($V_{oc}$) under typical indoor light. The solar blindness of the electrode enables a record-breaking bulk photovoltaic effect (BPE) with white light illumination (general use indoor light). This work opens up the perspective of ferroelectric photovoltaics which are not subject to the Shockley–Queisser limit by bringing into scene solar-blind conducting oxides.

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**1. Introduction**

A photovoltaic device generally requires at least one transparent conducting electrode for the light to reach the active light absorbing layers [1]. Although there has been recent interest in using correlated metals [2] and carbon-based materials such as graphene [3] transparent conducting metal oxides (TCO) based on degenerately doped In$_2$O$_3$, SnO$_2$ or ZnO and their alloys are currently the standard choice for transparent electrode applications [4–6]. These oxide semiconductors have bandgaps between about 3.1 and 3.7 eV, which make them “visible-blind” and suitable for applications requiring transmission up to the near-ultraviolet spectral range. Apart from being a fundamental element of a solar cell, such transparent electrodes are also hugely important for information and communication technologies such as displays, touch screens or light emitting diodes [7–9].

Amongst other semiconductor oxides, the monoclinic β-form of gallium oxide (β-Ga$_2$O$_3$) stands out because it has the widest band gap (~5 eV) among the practical TCOs and is transient down to ~260 nm, enabling improved “solar blindness” in photonic and photovoltaic applications [10–12]. Furthermore, owing to its extreme bandgap, doping control and critical electric field (~8 MV/cm), ultra-wide bandgap Ga$_2$O$_3$ is the platform of choice for the emerging fourth generation of power electronic devices after silicon, silicon carbide and gallium nitride [13–15].

In parallel to the development of β-Ga$_2$O$_3$ as a TCO, and so far, completely independent of it, there is a growing interest in the bulk
photovoltaic effect (BPE) [16]. This effect allows homogeneous solids with a non-centrosymmetric lattice (i.e. piezoelectric, pyroelectric and ferroelectric materials) to develop a steady photovoltaic current even in the absence of chemical potential gradients [17]. Excitingly, and unlike the classical semiconductor-junction photovoltaic effect, the BPE is not subject to the Shockley-Queisser limit and it allows photovoltages much larger than the bandgap. Consequently, extremely large photovoltaic fields of up to millions of Volts per centimeter can be expected [18]. Moreover, in the case of ferroelectrics, which are materials with persistent and switchable polarization, the sign and direction of BPE photovoltages and photocurrents may be inverted. Properly engineered, this kind of anomalous photovoltaic effect enables innovative energy conversion applications involving photons [19–21]. In practical devices, however, the photo-response should be generated by either the solar spectrum (outdoor natural sunlight) or indoor light (illumination without ultraviolet and infrared components), and therein lies a key issue: ferroelectrics that show above-bandgap photovoltages are generally wide-bandgap materials that only display a BPE response with illumination in the UV or near-UV range.

The recent approach to try to solve this problem has been to engineer ferroelectrics with a bandgap lying in the visible region in order to promote natural light harvesting [22–25]. Although Yang et al. [23] obtained visible anomalous photovoltaic effects in lateral structures (attributed to a domain wall tandem effect), the overwhelming majority of narrow-bandgap ferroelectric solar cells reported so far present disappointing photovoltages which are well below bandgap [26]. Crucially, no voltages greater than the bandgap have been reported in ferroelectric thin-film solar cells with conventional vertical structures (i.e. with a ferroelectric layer sandwiched between a top metallic electrode and a transparent superstrate electrode) – see Fig. 1-a, f - under solar/white illumination ([26] and references there in).

Here we show that adoption of β-Ga2O3 as the transparent electrode for BPE resolves this problem and allows a thin film solar cell with a conventional wide-bandgap ferroelectric (i.e. lead zirconate-titanate PbZr0.52Ti0.48O3 x = 0.53 or PZT) to display a giant BPE under white light. Therefore, with this approach we are able to break the S-Q limit for the maximum photovoltage in a sandwiched photovoltaic cell, as shown in Fig. 2-a,b. The solution process (described in methods) involved spin-coating of a Pb–Zr–Ti solution on the transparent electrode and an anneal in the temperature range of 550–650 °C (Fig. S1–S3). X-ray diffraction revealed the PZT films to be pure perovskite with a pseudo-cubic lattice parameter a = 4.077 Å, for both types of electrode (Fig. 2). The thickness of the PZT layers was ~90 nm (see methods). The optical bandgap of PZT was determined to be 3.6 eV using a Tauc plot, as described in methods (Fig. S4). Therefore, the PZT layer is indeed a wide-bandgap semiconductor where, in principle, photo-carriers could only be photo-excited under white LED illumination via absorption tail states that extend into the visible spectrum (Figs. S5–S7). Ferroelectric characterization via hysteresis loops (see Fig. 2-f) revealed large remnant (20 μC/cm2) and saturation (40 μC/cm2) polarization in the PZT.

Photovoltaic characterization was performed by current-voltage recording under illumination as described in methods. Ferroelectric poling was accomplished through a series of consecutive monopolar hysteresis loopings. A strikingly different photovoltaic behavior was observed for PZT/β-Ga2O3 compared to PZT/FTO, as shown in Fig. 3. While for PZT/β-Ga2O3 photo-current (jsc) and photo-voltages (Vmp) could be reversed by inverting the polarization, such a behavior was not observed for PZT/FTO. Importantly, the photovoltage was above bandgap for the PZT/β-Ga2O3 (Fig. 3-b), but well below bandgap for the PZT/FTO, which had a Voc smaller than 0.7 V. The above-bandgap photovoltages and their switchability for the PZT cells on β-Ga2O3 are both consistent with a BPE. In contrast, PZT/FTO did not show any sign of BPE (neither switching of photocurrent sign nor above-bandgap voltage) even after intensive testing of alternative poling routes or changing the PZT growth parameters (Figs. S9 and S10). The breaking-record maximum measured photovoltage for PZT/β-Ga2O3 was 6.6 V (Fig. 1-f), which translated into very large photovoltaic fields (EpV) of 0.7 MV/cm. As far as we know, this is the largest photovoltaic field observed for a ferroelectric under white light [30] and only second to antiferroelectric PbZrO3 under UV-light [26] (and references there in).

3. Discussion

3.1. A unique Ga2O3 transparent conducting electrode

The origin of this enhanced photovoltaic behavior with β-Ga2O3 electrodes are a combination of the solar blindness and the relatively low density of defect states in the gap due to the epitaxial and undoped (‘topological-like’) nature of the β-Ga2O3 film grown on r-sapphire. Here, the Ga2O3 transparent electrode is, in fact, the analogy of an extremely stable topological-like ultra-wide bandgap insulator, a solid that is a pure insulator in its bulk but has a metallic conductive surface. That conductive surface, in turn, was determined to be a two-dimensional conductive channel at the surface’s vicinity [27]. The nominally undoped epitaxial β-Ga2O3 thin films without any detectable defect showed the unexpectedly low resistivity of ρ ~ 3 × 102 Ω cm which was found to be also resistant to high dose proton irradiation (2 MeV, 5 × 1015 cm−2 dose) and was largely invariant (metallic) over the wide temperature range of 2 K up to 850 K. This high temperature stability is notable when compared with other correlated oxide systems such as confined 2D electrons at the metallic interface in between LaAlO3 and SrTiO3 [31] or in other oxide surfaces such as InO2, ZnO, TiO2, BaTiO3, SrTiO3 and CaTiO3 (and non-oxides e.g. InN). These oxides have also been reported to host a surface two
dimensional electron gas but presenting however air instabilities and, in general, practical electrical conduction only at very low temperature (i.e., <100 K) [32]. Therefore, the degree of novelty of this study is notable; not only is the first time Ga2O3 is used as a transparent conducting electrode within a (ferroelectric) solar cell architecture but this investigation represents, as far as we know, the first time a surface oxide’s 2D conductive channel has also been implemented in photovoltaics.

The origin of our Ga2O3 surface 2D conducting channel is still unclear. A number of high resolution techniques (including X-ray photoemission spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), secondary ion mass spectroscopy (SIMS), Rutherford backscattering spectrometry (RBS) and depth-resolved cathode-luminescence (CL)) did not reveal any bulk or shallow donor signatures that could explain the conductivity in terms of conventional impurity or defect doping. In the literature, a very
different nature of the bonding of interstitial hydrogen (H\textsubscript{i}) in Ga\textsubscript{2}O\textsubscript{3} compared to most other metal oxides has been suggested [33]. H\textsubscript{i} has been suggested to act exclusively as shallow donors in Ga\textsubscript{2}O\textsubscript{3} from theory and studies of the electronic analog muonium [34,35]. The bonding environment of the O atoms in Ga\textsubscript{2}O\textsubscript{3} results in O lone-pairs that may capture H\textsubscript{i} and form favorable shallow donors without much influence on the lattice, a phenomenon also exhibited by SnO\textsubscript{2}. Hydrogen is perhaps the only element that cannot be directly detected by XPS. In the experiment of Swallow et al. [33], the surface of an as-entered (201) Sn-doped (6 x 10\textsuperscript{18} cm\textsuperscript{-3}) Ga\textsubscript{2}O\textsubscript{3} crystal (from Novel Crystal Technology, Inc., Tamura Corporation) was indirectly found to be terminated by O--H groups, resulting in downward band bending of 0.24 eV and electron accumulation with a sheet density of ~ 5 x 10\textsuperscript{12} cm\textsuperscript{-2}. Their XPS O1s peak main component was associated with O bonded to Ga at 532.2 eV while a shoulder component (1.3 eV higher in binding energy), was associated with a hydroxyl (--OH) group. According to the authors, this is likely due to H-adatoms bonding to O atoms on the Ga\textsubscript{2}O\textsubscript{3} surface (surface adsorbates donate electrons into the surface accumulation layer [36]). Subsequent annealing (200–800 °C) reduces and eventually removes the shoulder component completely together with a O1s binding energy shift of ~0.7 eV to lower energy (531.6 eV). In our case, the 2D free electron concentration density profile for an undoped PLD thin-film (201) Ga\textsubscript{2}O\textsubscript{3} epitaxial on sapphire was estimated by the Thomas–Fermi approximation for a 2D system to be as high as n\textsubscript{s} ~ 2 x 10\textsuperscript{14} cm\textsuperscript{-2}. However, an analogous indirect analysis of the --OH groups by the O1s XPS peak shift has been determined to be smaller (~0.2 eV) [27]. (Surface) oxygen vacancies are other usual suspects for explaining the origin of oxide’s surface 2DEG due to local chemical doping (see e.g. Refs. [37–41]). Although there are many conflicting reports on the shallow versus deep nature of its related electronic states, oxygen vacancies would form well-localized, compact donors but this fact does not preclude the possibility of these states being shallow in nature, by considering the energetic balance between the vacancy binding electrons that are in localized orbitals or in effective-mass-like diffuse orbitals [42].

In contrast, commercial TCOs, such as FTO, have non-negligible absorption in the visible owing to their smaller bandgap and the existence of significant sub-bandgap transitions due to doping/defect-related states in the gap [43]. This is a problem for the BPE because the surplus of carriers that this absorption generates is injected into the ferroelectric (as depicted in Fig. 3 c–d), resulting in interfacial carrier injection that cancel out the BPE current [44]. In non-centrosymmetric materials, light quanta absorption provides an asymmetric energy distribution of non-thermalized photo-generated carriers. These photo-carriers lose their energy in descending to the bottom of the conduction band, which generates a shift in k-space and a BPE current [21]. The photo-carriers are further transported to the external connections by their respective TCOs, as depicted by their experimentally determined bandgap alignments (Fig. 3 c–d). While, for conventional photovoltaics additional TCO visible transitions are not a problem, they are a killer for the bulk photovoltaic effect for which any source of extrinsic conductivity is detrimental [17]. Whether a conventional degenerately doped Ga\textsubscript{2}O\textsubscript{3} TCO would preserve a gigantic bulk photovoltaic effect is yet to be determined. In this sense, Peelaers et al. [45] have already reported (by hybrid density functional theory)
sub-band-gap absorption bands when increasing the doping on Ga\textsubscript{2}O\textsubscript{3} above 10\textsuperscript{19} cm\textsuperscript{-3} owing to the enhancement of free carrier absorption (which also strongly depends on the polarization of the incoming light).

### 3.2. A bulk photovoltaic effect model

While there are theories about the origin of the bulk photovoltaic currents (in particular the so-called shift-current [46–48]), an accepted theory for the origin (and its related maximum magnitude) of the associated photovoltaic field is still missing (see e.g. Ref. [16]). This may be due to the fact that shift-currents are (somehow and sometimes) well explained by intrinsic phenomena (e.g. well-understood semiconductor band-to-band optical excitations) while their associated fields may be limited by a range of extrinsic effects such as lattice defects, dopants, interfacial barriers or the screening of the material’s polarization. To make things more complex, many of these defects (if not all) introduce levels within the absorber bandgap that may be photo-excited with a particular light energy (i.e., wavelength), a phenomena that sometimes is referred under the umbrella of photorefraction. The illumination wavelength is therefore critically important; while bulk photovoltaic effects are relatively common under near ultraviolet light (see e.g. the review in Ref. [26]) there are, to the best of the author knowledge, no demonstration in sandwiched photovoltaic structures under broad wavelength illumination such as white light or (simulated) sun light. A part of the absorber’s extrinsic defects/interfaces and the illumination spectra, the electrodes has a role. The observation of the electrodes affecting a ferroelectric photovoltaic device is indeed a very well-known effect (see e.g. Refs. [49,50]). For any photovoltaic device in general the choice of the electrodes (and/or buffer contact-layers) is critically important (the literature on this topic is huge - see e.g. Ref. [51] for a review for transparent conducting oxides and oxide buffers). So far, a change of electrodes in thin-film ferroelectric photovoltaic devices has been correlated with improvements in either photo-current or photo-voltage (or both). Typically, in these arrangements, such differences are explained in terms of modification of the Schottky barriers. Here, the changes in the photovoltage (more than 6 V) are simply too big to use conventional metal-semiconductor models. Besides, the photo-field of 0.7 MV/cm is much larger than any typical Schottky and p-n junction related space-charge field (typically ~10–100 kV). A tandem effect model does not hold. Notably, there is no appreciable developing photo-field characteristic time [18]. A photovoltaic developing time (in the range of few seconds to hours) is a typical signature of (near ultraviolet light) bulk photovoltaic effects [17] and, in turn, suggest a link with ionic drift, charge accumulation and polarization (switching) suppression [52–54]. If the photo-field upper bound is related with a pinned ferroic polarization, (the so-called Micheron criterion [55]), it would produce several MV/cm and ~100 V for a ~100 nm-thick layer, as already demonstrated in PbZrO\textsubscript{3} under near UV light [18]. If one assumes that the white light illumination is unable to produce structural polarization pining (or it has a much less actinic effect), it

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**Fig. 3.** (a) The PZT/FTO only exhibited a conventional photovoltaic effect signature in all cases with a photovoltage value (and sign) that did not depend on the polarization state and was always well below the PZT bandgap. (b) In contrast, above bandgap voltages were obtained for PZT/B-Ga\textsubscript{2}O\textsubscript{3} with photovoltages and photocurrents that were switchable via hysteresis loop poling. The large photovoltaic field associated with the Voc (6.6 V) of 0.7 MV/cm is generated with white-LED illumination. (c)–(d) B-Ga\textsubscript{2}O\textsubscript{3}'s wider bandgap and lower sub-bandgap absorption suppress both the TCO charge injection and the scattering event rates and thus provide the conditions required for the emergence of the BPE produced by white light. The experimental band structure was determined by UPS/UV–Vis (see methods).
is plausible to suggest that the experimental value of the photovoltage is determined by the amount of the ferroelectric polarization screening by photocurrents.

The experimental observation points out to the fact that the amount of screening is smaller with our undoped topological-like ultra-wide $\beta$-Ga$_2$O$_3$ electrodes [27] when compared to degenerately doped conventional transparent conducting oxides and, hence, the attainable open-circuit voltages much larger. From the Ga$_2$O$_3$/Pb(Zr,Ti)O$_3$ hysteresis loops we don’t see an appreciable amount of imprint (internal fields affecting the ferroelectric’s coercive field). The coercive field of our Pb(Zr,Ti)O$_3$ layers are typically $\pm$50 kV/cm, one order of magnitude smaller than the experimental photovoltaic field. Therefore, we might say that a local electric field due to the Ga$_2$O$_3$ metallic surface would be too small to explain the photovoltaic field. Other incongruence lies in the fact that the photovoltaic field is switchable; the Ga$_2$O$_3$ layer conductivity (or its surface band bending) cannot be varied after an electric field. Thus, we have no indication of imprint in the ferroelectric that may explain the differences in the photocurrent and photovoltage behavior but an often overlooked property of ferroelectrics is that a polarization switch implies a switch in the surface band bending. In traditional solid-state devices with classic semiconductors (e.g., silicon or SiC), their electrical behavior is strongly dependent on the size of various band offsets and Schottky barriers in the junctions of differing material (e.g. Refs. [56,57]). Owing to its ultra-wide bandgap, the band-offset in between Ga$_2$O$_3$ and Pb(Zr,Ti)O$_3$ would be smaller than the band-offset in between SnO$_2$ and Pb(Zr,Ti)O$_3$ [Fig. 3 (c) and (d)] but these contact barriers and offsets may dramatically change depending on the ferroelectric polarization. It is well-known that chemical and structural factors can alter transition-metal oxide work functions. In particular, the ferroelectric photovoltaic phenomena would represent the kind of system where surface electric dipoles, absorbants and surface band bending play a major role [58–60]. It is also very well-known that the engineering of any metal-oxide work function within a solar cell architecture would show a direct correlation with the solar cell performance (e.g. Ref. [61]). In thin-film photovoltaics, in general, the low doped (intrinsinc) absorber or the barrier extraction layers (either n-type or p-type) conductivities do not change. Either, a n-i-p or p-i-n configuration establishes the direction of the photocurrent by engineering the band-offset alignment [51]. The photocurrent flows to the outer electrodes when electrons shift to lower energies while the holes shift to higher energies (respect to the vacuum level). In the bulk photovoltaic effect with Ga$_2$O$_3$ transparent conducting electrodes reported here, the band bending of the Pb(Zr,Ti)O$_3$ interfaces may be reversed by an external electric field so that a switchable photocurrent may still be impressed which direction depends on the ferroelectric polarization [Fig. 4] [44]. This effect is lost when the ultra-wide bandgap Ga$_2$O$_3$ transparent conducting oxide (TCO) is replaced by a conventional TCO (SnO$_2$:F or FTO in this case), arguably because conventional highly doped TCOS aren’t, indeed, totally transparent but they photogenerate parasitic carriers that effectively screens the absorber polarization. Here, we want to stress again that, for the Ga$_2$O$_3$ layer, a number of high resolution techniques (XPS, EDS, SIMS, RBS, CL) did not reveal any bulk or shallow donor signatures that could explain the conductivity in terms of conventional impurity or defect doping. Or in other words, it has been proven to be difficult to optically excite any “impurity center” in our topological-like Ga$_2$O$_3$, a kind of “super-transparency” so to speak.

In either case, there is no evidence of rectifying behavior at the interfaces [52]; we have not measured a single exponential J-V curve (dark or under illumination) but typically quadratic or linear J-V curves. Our FTO or GAO based solar cells aren’t limited by a Schottky contact [63] but their transport mechanisms are rather bulk limited [64]. Both metal electrodes may form Schottky interfaces to the PZT, especially if their work-functions vary depending on the ferroelectric polarization band-bending. However, if there is accumulation of charges at the interfaces, the Schottky depletion region is drastically thinned to the point to be in the tunneling contact regime (or field-emission) [65] and the absence of rectifying contacts is typical of the classic bulk photovoltaic effect. Indeed, the white LED photovoltaic curve is well fitted using a simple Mott-Gurney (also known as space-charge) transport law [66]. $J = V(AV^2) - J_p$, where $V = V/|V|$ and $J_p$ is the photovoltaic current. Either, in the low field limit and in the saturation regime limit, the space charge current becomes linear with the field. The space charge limited transport is typical of sudden free-charge injection in insulators (in conducting solids the free charges are quickly neutralized, screened or drained) and therefore consistent with a bulk limited transport mechanism. A is a constant that has been found to be asymmetric depending on the polarity of the voltage, i.e., $A^+$ and $A^-$ (see supplemental materials). The asymmetry is indeed usual in any non-ideal insulating thin-film; there is a frequent departure from the ideal law owing to defects and/or non-ideal injection regions [67]. The space-charge current asymmetry is also dependent on the effective dielectric constant (i.e., polarization variation with respect to an applied field) which is non-linear in ferroelectrics, assuming invariant electron mobility. It also further supports the hypothesis of the origin of the above bandgap voltages being unrelated to Schottky barriers or work functions but with a continuum of photo-generated space charges within the film. Even if an ad-hoc model is out of question, a qualitative expression can be derived taking into account the space charge hypothesis. In the open-circuit condition, $(AV^2) = J_p$ or $(B/V_j)_p = J_p$, where in the ideal case, the Mott-Gurney B constant is $B = 8\mu/9L^2$, $\mu$ is the dielectric constant, $\nu$ is the mobility and $L$ is the slab thickness. The definition of the dielectric constant is $\epsilon = 1 + \partial\rho/\partial E$ and in ferroelectrics $\epsilon$ is much larger than the unity
and therefore, \( e = \partial P / \partial E \). Thus, an expression can be derived for the open-circuit voltage as,

\[
V_{pv} = \sqrt{\left(1 + \frac{\partial P}{\partial E}\right)^{-1} \sqrt{J_{pv}/B}}
\]

Assuming that the second term \( \sqrt{J_{pv}/B} \) is independent of the transparent conducting oxide acting as electrode, the space-charge photo-voltage depends on the amount of screening of the polarization or polarization pinning. In the case of neutralizing charges being injected into the ferroelectric, the polarization is screened \((1 + \partial P/\partial E = 1)\) and the space-charge field remains low while if the polarization remains pinned a much larger photovoltage may be developed.

3.3. Future outlook

From a photovoltaic point of view, the most important result is that a giant BPE was obtained for a standard (wide-bandgap) ferroelectric under white light illumination (rather than with the near ultraviolet illumination that is generally required to produce a BPE in such ferroelectrics \([18,30,68]\)). It is proposed that even bigger BPE currents could be possible by combining inorganic polar materials, such as LiAsSe2 \([69]\), and organic compounds, such as conjugated vinylene-linked hybrid heterocyclic polymers \([70]\), with solar blind transparent conducting electrodes to preserve the effect.

Ga2O3 is a rising star amongst emerging ultra-wide bandgap semiconductors for solar blind transparent conducting electrodes \([14]\). Recently, Ga2O3 is receiving a lot of renewed attention as a semiconductor for solar blind transparent conducting electrodes \([14]\). Ga2O3 exhibits BPE effects and switchable transparent properties \([71]\), large tuneable bandgap value was determined to be 3.6 eV. The synthesis of the PZT was done as follows: Zr-isopropoxide (Zr(OC(2H5))4 -70 wt % in 1-propanol- Sigma) and Ti-isopropoxide (Ti(OC(2H5))4 (97%) Sigma) were mixed. Afterwards, acetic acid and n-propanol were added to the Zr/Ti solution. Then, Pb acetate (10x excess) was dissolved in trihydrate, Pb(CH3CO2)2·3H2O (99.999%) was dissolved into the above solution heating the solution in a silicon oil bath to 85 °C for dissolving the Pb precursor completely. After the cooling, down of the solution, acetic acid and distilled water were added to modify the Pb-Zr-Ti solution and adjust the solution to make 40 ml 0.4 M.

The GAO epitaxial TGO growth method is described in the previous section. The FTO substrates were bought from Solens, model ASAH! 100 by CV of 1.1 mm thickness, (70-100-Q resistance, thickness of FTO layer 800 Å.) were cleaned with soap water, milli-Q water, ethanol (99.5%) for 20 min before use. After an UV light cleaning step for 20 min, 80 ml of PZT solution was spin-coated on top of the GAO or FTO at 4000 rpm with an acceleration of 2000 rpm for 40s. The solution was dried in the hot plate for 5 min at 150 °C. The PZT layer was further annealed (400–650 °C) and/or oxidized (550–650°C), for 10 min in air and/or 2 h in oxygen, respectively. Finally, a layer of 100 nm of the Ag metal was evaporated on top of the PZT layer in a BOC Edwards Auto 306 thermal evaporator. Devices were patterned using shadow masks with device area lying in the range of 3x10 -4-0.2 cm².

5.3. Characterization

X-ray powder diffraction (XRD) analyses between 5 and 120° in a RIGAKU Rotaflex RU200 B instrument, using CuKα1 radiation.

X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) measurements were performed with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany) in ultra-high vacuum conditions (base pressure 3 E-10 mbar). XPS measurements were performed with a monochromatic K alpha 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.

Light-emitting diode (LED). The White-LED (W-LED) measurements were carried out in a home-made set-up attached to a probe station. The W-LED source is a commercial LED 3 x 1 W and 360 lm (lumens). The total irradiance has been determined to be \( I = 888.9 \) W m⁻² and in the blue peak \( I_{blue} = 266.7 \) W m⁻². 1–I curves were measured with a Keithley model 6430 Sub-Femtoamp Remote SourceMeter.

Spectral Irradiance measurements were performed with a spectrophotometer SPECTRO 320 (D) release 5, 30932004, with gadget EOP-146 to measure the spectral irradiance. Spectral irradiance has been measured out-of-plane (90°) with a scan step of 1 nm and a speed of 100 ms/nm.

The UV–visible analysis of solutions and thin films were made in a Shimadzu 1800 spectrophotometer. The optical band gap was derived from the Tauc’s relation: \( a h v = A(h v - E_g)^{1/2} \). Where, \( a \) is the absorbance, \( A \) is a constant, \( h v \) is photon energy, \( E_g \) is the allowed energy gap and \( \eta = \gamma \) for allowed direct transitions. The PZT optical band gap value was determined to be 3.6 eV.
The ferroelectric characterization was performed with a precision LC tester LCII Ferroelectric Test System unit of radiant technologies attached to a probe station.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtener.2019.100350.

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