Effects of a flexible ion gel as an active outer-layer when in contact with a metallic electrode

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Received: 25 March 2022 / Accepted: 7 June 2022 / Published online: 5 July 2022
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Abstract
In this work, the effect of an ion gel outer-layer stuck on top of ITO/PBT/Sn devices was investigated towards its effects on the electrical properties. When this external electrolyte film is in contact with any top permeable electrode, it produces a self-biasing effect and changes the charge carriers' injection properties. The outer-layer promoted situations where the output current increases up to two orders of magnitude and others where the output current decreases one order of magnitude in comparison to the same samples without it. Admittance spectroscopy measurements were made and the proposed equivalent circuit model indicates that the interfacial electrical properties dominate charge carrier injection face the bulk properties when the outer-layer is present. All the changes observed here are reversible after the ion gel is detached and replaced, indicating that ions do not diffuse into the active layer. The observed results can contribute to improve the current density in certain sandwich structures as well as notify that electrolyte external films can behave as an active layer promoting electrical changes into sandwich devices and can be extended to cases where the electrolyte film is used as substrate.

Keywords Self-biasing · Ion gel outer-layer · Electrolyte interface · Permeable metal contact

1 Introduction
Many optoelectronic devices are based on vertical stacked layers forming a sandwich structure, such as light-emitting diodes (LEDs) [1], light-emitting electrochemical cells (LECs) [2, 3], electrochromic devices [4], solar cells [5], vertical transistors [6–8], among others. The efficiencies of these devices depend on many different conditions. One is regarding to the control of the density of charge carriers available inside the active layer. Different electrical properties could provide higher or lower charge carrier density flowing throughout the device as, e.g., charge carrier mobility from the semiconductor or energy-level alignment at the interfaces. This second example can be improved by playing with the energy-level matching at the interface of two different materials that can be semiconductor/semiconductor (S/S) or metal/semiconductor (M/S) interfaces [9–12].

There are different strategies used to align or tune the energy levels at the interfaces: control of molecular orientation which essentially promotes an energy offset between the materials [13]; self-organized low work function cathode interlayer created from blend solution [14]; control of dipolar packing coverage which abruptly shifts the interface electrostatic potential [15]; addition of monolayers at the interface with covalent bonding to one or both interface materials which alters charge carriers distribution [16]; or even it is possible to find interesting works providing a broad overview and perspectives of tuning the energy-level alignment at interfaces between inorganic and organic semiconductors [17] and/or exploring interface engineering to play with the energy-level alignment [18]. However, all these strategies involve interface modifications by acting on the active layers, inside the devices.

Adding an interlayer between M/S interfaces is a common technique to improve charge carriers injection [9, 10,
19], but not necessarily something easy to achieve in practice. Interlayers change the energy barrier for charge carriers injection by the creation of a metal/interlayer/semiconductor (M/I/S) structure [20]. The M/I/S structure is more frequently obtained from sequential layers deposition (or step-by-step preparation) [21]. It is also possible to obtain this structure from blend solution composed by the active layer and interlayer materials, where the interlayer material spontaneously segregates onto the electrode (cathode or anode) forming the M/I/S structure [14, 21]. The deposition procedure of an interlayer presents difficulties like the compatibility with the previous and/or coming layer regarding to solvent, temperature, deposition techniques, and accuracy control of very thin thickness, besides to increase production time and cost of fabrication.

Latest studies depict that the interlayer and/or the active layer can be added by ionic species resulting in ionic-electronic doping [22–25]. It promotes a significant band bending change in the semiconductor electronic structure. However, it can result in ion diffusion throughout the semiconductor that promotes ionic doping and/or electrochemical processes. The control of these situations is still challenging, once it can promote oxidation (or reduction) states at the electrodes/semiconductor interface and, consequently, degradation of the semiconductor [22, 26].

In this work, it is proposed a differentiated technique where the electrical properties of a metal/organic semiconductor interface can be modified by ionic species localized not as an interlayer at this interface but as an outer-layer outside the device. The outer-layer is composed by a flexible ion gel film and it is stuck on top of the sandwich structure metal/organic semiconductor/metal. Since the outer-layer is composed by a dry film stuck externally on the device, the present technique does not face the difficulties experienced by the interlayers deposition like the compatibility of solvent, temperature, deposition techniques, and accuracy control of very thin thickness. The ion gel outer-layer is able to change the charge injection throughout the device increasing or decreasing the output current intensity depending on the thickness of the electrode in contact with the ion gel. This external and flexible electrolyte layer is formed by an ionic liquid immobilized inside a polymer matrix and the ion diffusion into the semiconductor is avoided, since it is an outer-layer. It is expected that the analyzed effects here can be extended to any device with an ion gel film stuck on any top electrode (or under any bottom electrode). The main observed phenomenon was analyzed as a self-biasing effect [27] able to improve (or reduce) the efficiency of charge carriers’ injection throughout sandwich structure devices.

2 Materials and methods

2.1 Materials and films’ preparation

The bottom conductive electrode is composed by indium tin oxide (ITO) with 15 Ω/square sheet resistance purchased from Luminescence Technology Corp. (LUMTEC). In the sequence, a 250 nm thick poly-bithiophene (PBT) was electrochemically synthesized over ITO, based on the same procedure described elsewhere [28]. The top permeable electrode is composed by an evaporated Sn layer with a deposition rate of ∼15 s⁻¹, controlled during deposition with a crystal quartz oscillator. Three different thicknesses layers were obtained and studied.

The electrolyte outer-layer is composed by a flexible ion gel film produced from acetone solvent, poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ([EMIM][TFSI]). The ion gel solution was prepared based on the weight ratio between polymer:ionic liquid:acetone of 1:4:7 [29], respectively. The solution was stirred at 40 °C for 40 min, 130 μL were drop casted in an area of ∼(1.3 × 2) cm² of a pre-cleaned lime glass slide and awaited 30 min for drying. After that, the ion gel films were cut and stuck on the permeable electrode with tweezers [29], similar and easy as manipulating a sticker.

2.2 Device fabrication and characterization

The explored architecture was a vertical sandwich structure metal/polymer/metal composed by ITO/PBT/Sn whose pattern is depicted in Fig. 1a. After that, an ion gel outer-layer was easily stuck on (or removed from) the top of this structure (Fig. 1b). It was also produced a non-usual device structure with stacked layers of ITO/PBT/ion gel, where the ion gel replaces the role of the top electrode (Fig. 1c).

The electrical characterization was performed using a Keithley 2602 dual-source meter and an Agilent 4284A Precision LCR meter instrument in dark ambient atmosphere.

![Fig. 1 Devices structures: a ITO/PBT/Sn; b ITO/PBT/Sn/ ion gel and; c ITO/PBT/ion gel, where the ion gel replaces the role of the top electrode to provide us a reference-line output current.](image-url)
and room temperature, setting Sn or ion gel as the common electrode. AC measurements were performed by applying an AC voltage of 0.5 V and a null DC voltage. The equivalent electrical circuit simulations of admittance spectroscopy were performed in Matlab considering surfaces/interfaces and bulk properties of the semiconductor as, e.g., traps energy levels. Scanning electron microscopy (SEM) images were obtained in a VEGA3 LMU TESCAN microscopy. The layer thicknesses were measured by a Bruker Dektak XT profilometer.

3 Results

Evaporated Sn films are oftentimes used to produce permeable electrodes due to its grained profile. The porosity depends on its thickness, evaporation rate, and roughness of the substrate [6, 30–32]. To analyze the effect of the ion gel in contact with a metal layer, three different Sn thicknesses layers were produced, named: (i) thin (~ 128 nm); (ii) intermediate (~ 264 nm) and thick (~ 350 nm) layer. SEM images from the three different Sn thicknesses are shown in Fig. 2:(a) thin, (b) intermediate, and (c) thick Sn films on PBT (left side) and on glass substrate (right side). These images were obtained at the PBT/glass frontier and close to this region. The same Sn contact displays relevant differences between grain percolation on top of PBT layer and on glass substrate. The three Sn film thicknesses on PBT semiconductor show pores whose profiles are: (a) low percolation paths with high porosity, (b) high percolation paths with high porosity, and (c) high percolation paths with low porosity. These percolation profiles will be correlated with the $I–V$ measurements from Fig. 3 in the sequence. For the three samples, there is also percolation among the Sn grains on glass substrate, as desirable to produce good electrode/contact with a small amount of pore distribution. The main goal of this work is to analyze the effects of the ion gel to the organic semiconductor/metallic electrode. It is important to emphasize that the thickness of the PBT was not varied, because the sequences of results that will be presented show that the effect of the ion gel outer-layer is on the Sn/PBT interface and not on the PBT bulk. XRD analysis was performed on a device consisting of glass/ITO/PBT/Sn structure showing its polycrystalline Sn film profile (see more details in Fig. 3 in the supplementary material).

Figure 3a–c shows $I–V$ curves for bipolar bias of ITO/PBT/Sn device without and with the ion gel outer-layer. From PBT, polymer is expected that positive charge carriers dominate charge transport on both bias. The ion gel layer is composed by a polymer with dielectric properties and, in spite of that, it is possible to quantify a non-negligible electric current along the ion gel film. Therefore, it was also developed a non-usual structure for electrical characterization that is ITO/PBT/ion gel as depicted in Fig. 1c where the ion gel layer is used as an electrode. It will provide us a reference-line output current and its $I–V$ curve is depicted in Fig. 3d, having no other purpose or functionality in electronics in its present form.

ITO and Sn work functions are ~ 4.7 eV [33] and ~ 4.4 eV [6], respectively (see flat band energy diagram in supplementary material). PBT’s HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels are reported as ~ 5.3 eV and ~ 3.3 eV, respectively [34]. PBT is a p-type semiconductor and this device depicts a hole charge carrier transport with an almost symmetric energy barrier level for holes injection from both electrodes. The lower energy barrier is for ITO/PBT with ITO as anode. The higher energy barrier injection is related to the Sn/PBT interface, whose interface properties will be changed by the use of the proposed ion gel outer-layer. It shows an almost symmetric energy barrier level for hole injection from both electrodes with a lower barrier for ITO as anode. The $I–V$ measurements confirms it as shown in Fig. 3b, c for structure ITO/PBT/Sn (black squares symbol) and ITO/PBT/ion gel (red circles symbol). The asymmetric $I–V$ curve from 3(b) is attributed to the grained Sn profile that reduces the active area of contact.

For the non-usual structure of ITO/PBT/ion gel outer-layer, the $I–V$ measurement is depicted in Fig. 3d providing us a base-line output current. The current intensity in this case is limited by the leakage current throughout the ion gel film. The same ion gel film is widely used as gate dielectric layer in electrolyte transistors [8, 29, 35] and it could induce the reasoning that, as an insulator, any current through it would be negligible. Therefore, this base-line output current provides one of the evidences that the ion gel film acts as an active layer. The rectifying behavior is attributed to the fact that at forward bias, the ITO electrode works as an infinite charge carriers’ reservoir that easily inject holes through a low-energy barrier. However, for reverse bias, holes are poorly drifted throughout PBT film, proportionally to the amount of the accumulated holes at the ion gel/PBT interface. Note that the accumulation layer is formed on the semiconductor surface due to the ions polarized along the ion gel under external bias with a distribution similar to that observed, e.g., in field effect transistors when ion gel is used as a dielectric layer [23].

For samples with thin Sn thickness, Fig. 3a, the output current intensity for ITO/PBT/Sn structure is lower than for ITO/PBT/Sn/ion gel one, at forward bias. It can be explained by the conduction along the ion gel film which is higher than along the thin Sn film with low percolation paths, depicted in SEM images (Fig. 2a). This statement comes from comparison of the output current from Fig. 3a, d (red circles symbol) that present the same output current intensities. For reverse bias, the current intensity is higher for the sample with the thin Sn contact than for ion gel as contact. That behavior is
Fig. 2 SEM images of evaporated Sn films on top of PBT (left side) and glass substrate (right side) for different Sn film thicknesses named: 

- a thin (~ 128 nm)
- b intermediate (~ 264 nm)
- c thick (~ 350 nm)

Fig. 2 SEM images of evaporated Sn films on top of PBT (left side) and glass substrate (right side) for different Sn film thicknesses named: a thin (~ 128 nm); b intermediate (~ 264 nm) and c thick (350 nm).
expected, since, even with low percolation paths, the Sn film is metallic and contributes to the charge carrier injection, which does not happen when the ion gel is used as a contact.

Figure 3b shows the $I$–$V$ curve of the device constructed with intermediate Sn thickness. The output current increases $\sim 10^3$ orders of magnitude at reverse bias and there is a small change for forward bias when compared to the sample with thin Sn thickness without ion gel. The changes are attributed to the higher number of percolation paths throughout the Sn film that provides a lower sheet resistance to the contact (see images in Fig. 2b). When the ion gel is stuck on the permeable Sn film, the output current decreases for forward bias, while it increases for reverse bias, compared to the same sample with and without ion gel outer-layer. To explain this phenomenon, it is necessary to note the role of the pores in the Sn film that allows the ion gel to stay in direct contact with PBT film in some regions. In these pores' region, the polarized ions into the ion gel will induce charge carriers on the semiconductor surface. At forward bias, electrons are induced in these pores and will not contribute to increase the output current, since PBT is a p-type semiconductor. The decrease in current intensity is attributed to an effective sheet resistance that now occurs along the Sn and ion gel films.

A noteworthy result to be considered on applications of any vertical architecture device whose ion gel film could be placed in contact with a permeable electrode is the analysis of the current increase under reverse bias in Fig. 3b. The
intensity of the output current depends on the effective charge carrier injection regions from the permeable electrode, formed by: (i) Sn grains acting as percolated paths when a voltage is applied and (ii) the Sn pores' region where charge carriers are induced on the semiconductor surface when ions are polarized under external bias. When reverse bias is applied, anions are polarized at the pores region and positive charge carriers are induced on the semiconductor surface, forming an accumulation layer. Therefore, the output current intensity is a sum of: (i) the current from the regions where there are percolated paths along the Sn grained film (current created by charge carriers injected by the metallic Sn grains) and, (ii) the drift current from the accumulation regions into the pores. This phenomenon created by the polarized ions within the pores of the electrode can be named as self-biasing effect [27], once it is equivalent to an external applied bias able to improve the output current density.

This kind of exploring self-biasing could provide an alternative way to improve the density of charge carriers into the device without the need to improve the voltage range. Another technique often used to increase current density in devices is the addition of an interlayer able to improve the energy-level mismatch at the injection/collector interface. Interlayers improve charge carriers injection in devices, but presents limitations due to the compatibility of sequential deposition processes like solvent or temperature as required from sequential deposition [12, 21]. It is important to note that the microscopic effects between that created by an interlayer and the present proposal with an outer-layer are quite different. Nevertheless, an outer-layer can bring similar macroscopic results with an easy step deposition of an external dry layer.

Figure 3c presents $I$–$V$ curves of the device constructed with thick Sn thickness. The output current presents similar behavior at forward bias when compared to the sample with an intermediate Sn layer, indicating that both Sn layers are good collector contacts. For reverse bias, the current is increased when compared to the sample with intermediate Sn thickness, possibly due to the higher number of percolation paths in the Sn grained film that improve the injection active area of the device under this electrical setup. When the ion gel is stuck on the sample with Sn thick film, the output current decreases for voltage ranges greater than 2 V. The SEM images provide information of a permeable Sn film on PBT semiconductor and profilometer measurements provide the information of a Sn thickness film of ~ 350 nm. This couple of particularities bring forth the guidance of a low probability of the ion gel being in direct contact with the semiconductor into the porous. The electric field created by the polarized ions into the pores will be blocked by the thick metallic layer. However, the ionic gel layer still brings changes to the intensity of the output current, whose phenomenon should be considered whenever an ion gel is used in contact with an electrode of any device structure. For a better understanding of the phenomenon, admittance spectroscopy was performed on these devices and equivalent circuits are proposed comparing the device with and without ion gel outer-layer. The results are showed in Fig. 4.

Even when very thick Sn layers were used, some electrical properties of the sandwich structure showed changes due to the ion gel outer-layer. That phenomenon is not necessarily expected once the metal contact can shield the electric field created by ions. To understand the role of the ion gel outer-layer on sandwich structure, AC measurements were performed to observe the dependence of the frequency-dependent admittance for the device structure with thick Sn layer and without the ion gel outer-layer. Considering these results, a simulated equivalent circuit is proposed to extract information based on physical concepts.

Simulation parameters were based on experimental data provided by Souza et al., where thermally stimulated current method (TSC) was used to analyze trap levels inside PBT active layer devices [28]. In their study, the authors obtained at least three different traps energy levels that support the proposed simulation parameters. Bulk and/or interface characteristics were investigated based on admittance spectroscopy method. In parallel capacitance ($C$) and resistance ($R$), admittance is defined by [36]

$$Y = G + jωC;$$

where $G = 1/R$ is conductance, $ω = 2πf$ is angular frequency, and $f$ is frequency. Roberts and Crowell [37] have described that each trap level in inorganic semiconductors acts as capacitance and resistance associated in series, and any additional trap levels are associated in parallel. This information was considered in our simulations. The PBT-based device without ion gel would, then, be represented as in Fig. 4a, where $C_1$ and $R_1$ represent bulk parameters of PBT film and $C_2$, $C_3$, $C_4$ and $R_2$, $R_3$, and $R_4$ are capacitances and resistances, respectively, of the three traps energy levels provided experimentally in the literature [28]. The circuitry parameters are used to simulate frequency dependence of the Loss ($G/ω$) and frequency dependence of the capacitance ($C$) curves, as shown in Fig. 4b. The simulated curve depicts good agreement with the experimental results, being the broader loss peak associated with more than one energy level for traps. It is important to note that, according to Souza et al [28], some trap levels on PBT do not have a discrete energy level as simulated in the proposed equivalent circuit of Fig. 4a, but present a broad and possibly not homogeneously energy distribution, that can explain the small deviation between simulated and experimental curves.

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Since the main goal is to understand the effect of the ion gel outer-layer on the device, a more complex circuit was not simulated.

The admittance spectroscopy measurements for the device without and with ion gel outer-layer presented considerable changes (see, Fig. 4b, d, respectively). The proposed equivalent circuit to fit the data from the sandwich structure with ion gel is shown in Fig. 4c, where $C_{\text{int}}$ and $R_{\text{int}}$ are capacitance and resistance, respectively, of the PBT/Sn interface, and $R_g$ is associated to the effects of the ion gel outer-layer on overall device resistance.

Experimental and simulated data have good agreement. Simulated parameters provide the information that now the interface dominates the electrical properties of the device in contrast to the previous one. From these results, only a possible relaxation was fitted at low frequencies due to the dominant effect of interface states, changing the behavior of both capacitance and loss. It is a noteworthy result considering the thickness of Sn layer ($\sim 350 \text{ nm}$) and even so the ion gel has the capacity to dominate the resistance and suppress the effect of traps, which is a PBT bulk property, changing completely the AC electrical characteristics. Equally important is the fact that this is accomplished with no ion doping of the semiconductor, e.g., by ion diffusion from the ion gel outer-layer into PBT, as indicated by sequentially electrical measurements performed on attached and detached gel layer (see supplementary material), avoiding oxidation and degradation of the device generated by ionic species when they are used inside the sandwich structure.

In summary, the effects of the ion gel on the three different thicknesses are: for thin Sn film: the current increase to forward bias due to a reduction of the sheet resistance, since the resistance of the ion gel film is lower than the Sn film that has just a few percolation paths. For the current under reverse bias, almost no change is observed, because it is expected that the metal has the majority contribution to the charge carrier injection into the polymer; for intermediate Sn film: the current decrease to forward bias owing to the induction of negative charge carriers into the pores of the permeable electrode creating a depletion region reducing the electrical transport. Due to the depletion region, the self-biasing reduces the charge carriers transport. For the reverse bias, an increase in current is observed, because induced positive charges form an accumulation layer into the pores of the permeable electrode. Due to the accumulation region, the self-biasing enhances the charge carriers transport; and for thick Sn film: small decrease in both forward and reverse bias current at higher voltages showing that the ion gel can be an active outer-layer even for thicker electrodes once that under this configuration, the interface dominates the electrical properties of the device.

It is plausible to suppose that these results can be extended to situations where an ion gel film is used also as

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**Fig. 4** a Equivalent circuit and b AC measurements and simulation of ITO/PBT/thick Sn device. c Equivalent circuit and d AC measurements and simulation of ITO/PBT/thick Sn/ion gel device. AC measurements are frequency dependence of the loss and frequency dependence of the capacitance.
a substrate (bottom outer-layer). These results can also be considered on many other devices, such as diodes cells, solar cells, and even as a partial structure of vertical electrolyte transistors, since the architecture studied here depicts similar base geometry structure for these devices. This study aims to provide an understanding about the advantages that can be obtained with the use of an ion gel outer-layer.

## 4 Conclusion

Interface engineering is a useful strategy to improve device efficiency and it can be exploited through modification by electronic and/or ionic conduction through the involved materials at the interface. Commonly, changes in the electrical properties of interfaces are made by modifying/adding internal layers to devices. In this work, it was shown that the use of an ion gel outer-layer is also able to modify the charge carriers’ injection. The outer-layer is easily stuck externally over a sandwich device architecture, not having deposition limitations such as solvent or temperature deposition sequence compatibility. Depending on the thickness and porosity of the electrode that is in contact with the electrolyte film, different effects were observed. Under the limit of the analyzed Sn electrodes thicknesses in this work, changes were observed in the output current intensity. It means that the ion gel works as an active external layer. The most significant result is the improvement in the output current for reverse bias for the sample with an intermediate Sn film, promoted simply by the presence of the ion gel outer-layer due to a self-biasing effect created by the presence of ionic species in the outer-layer. Impedance spectroscopy measurements indicate that the effects of the ion gel on the PBT/Sn interface are able to dominate the electrical characteristics of the device against other interfaces or the polymer bulk. It happens even for metallic electrodes as thick as ∼350 nm, by suppressing the effects of interfacial traps without ion doping or diffusion to the polymer. This easy and cheap technique can be applied in a huge variety of sandwich structure devices as a simple method to modify charge carriers’ injection, since the ion gel can be used on top (or under a bottom) of any permeable electrode.

## Acknowledgements

The authors would like to thank CME/UFPR for technical support on SEM experiments and Fabiano Yokaičiya e Guimther Kellermann for technical support on XRD experiments. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES)-Finance Code 001.

## Author Contributions

EAM and ACP have done the fabrication of the devices, electrical characterizations, and validation; ARVB has performed the equivalent circuit simulations, methodology, and writing; JPMS has provided resources, funding acquisition, methodology, supervision, helped in experiments, and writing; KFS provided the conceptualization, project administration, co-supervision, methodology, helped in experiments, writing, and editing.

### Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Declarations

### Conflict of interest

Authors declare no conflicts of interest

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