# Effect of the interfacial dipole layer based on glycine on the electrical characteristics of organic Thin-Film Transistors

Carme Homs Pons, José Javier Ruiz, and Nicolás Sibuet Ruiz
*Enginyeria Física, Universitat Politècnica de Catalunya*
(Dated: May 28, 2018)

A dipole layer made of amino acids has been implemented in organic thin-film transistors (OTFTs). The chosen amino acid was glycine, since it has the greatest dipole moment. Pentacene, a p-type semiconductor, was used for the active semiconductor layer. Results clearly show that glycine layer affects the performance of manufactured devices. A 5 V shift in threshold voltage has been observed when a 20 nm glycine layer was considered in a BGTC organic transistor. Minor changes in mobility and intensity have also been observed. Experimental results indicate that the shift of the transfer characteristics is governed by the addition of a layer of amino acids. This would mean that threshold voltage shifting could be controllable by adding a dipole layer.

## I. INTRODUCTION

A transistor is a three-terminal electronic device in which electric current flows within a channel between two terminals (source and drain) and is regulated by a third terminal (gate). Threshold voltage is defined as the voltage that must be applied on the gate so that the conducting channel is formed. In such case, current will flow if voltage difference between source and drain is applied.

Thin-film transistors (TFTs) are transistors which have been fabricated by placing thin films of an active semiconductor layer, a dielectric layer and metallic contacts over a suitable conducting substrate. For instance, they are widely used in flat panel displays. In addition, organic thin-film transistors (OTFTs) are TFTs that use organic semiconductors as active layers and have many advantages such as biocompatibility and flexibility, leading to promising applications for bendable displays and chemical and biological sensing.

Threshold voltage shift in organic transistors has been achieved by using self-assembled monolayers (SAMs), which are still being investigated [1,2]. Herein, it is proposed the use of amino acids (organic molecules) with a strong dipole for the same purpose. It can be also thought in the opposite direction: it may be possible to characterize the dipole moment of the amino acid from the threshold voltage shift.

As a first step, only glycine has been considered, due to the fact that it has the strongest dipole over all the amino acids and it is expected to show more remarkable results. Pentacene-based OTFTs have been manufactured and characterized in order to study differences in performance when a glycine layer is present and when it is not. To the best of our knowledge, amino acids have been tested in solar cells but not in OTFTs, so, if results are positive, this first step could lead to a new line of research.

Three pairs of devices were manufactured, one device of each pair containing glycine and the other not. It was decided to try both Bottom Gate-Bottom Contacts (BGBC) and Bottom Gate-Top Contacts (BGTC) configurations. BGTC configuration was expected to show better results as charge carriers do not have to cross a glycine layer to go from the contacts to the semiconductor. Thus 2 pairs of devices with BGTC configuration were manufactured: one with a glycine layer of 5 nm thickness and the other with 20 nm thickness, and one pair with BGBC configuration with a glycine layer of 5 nm thickness. All devices were constructed over a crystal silicon (c-Si) flat substrate, with a thermally-grown silicon dioxide ($SiO_2$) layer provided by FRAUNHOFER IPMS and pentacene -an organic p-type semiconductor- was used for the active semiconductor layer.

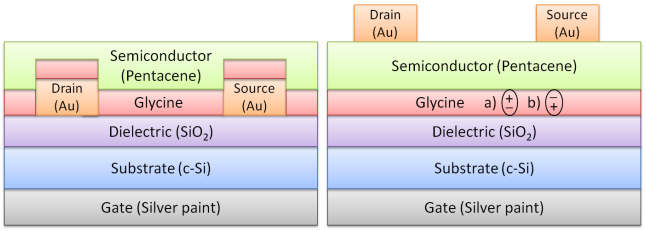


FIG. 1: Diagram of an OTFT with a glycine layer. (Left: BGBC configuration. Right: BGTC configuration.)

FIG. 1 shows the structure of fabricated BGBC and BGTC configurations but dimensions are not to scale, i.e. thickness of c-Si is 250 $\mu$m and thickness of dielectric is 120 nm. Current takes place in the semiconductor layer, where a p-channel is formed. Because of the polar nature of glycine, a potential difference across its layer is expected to appear, which probably depends on how the molecules are oriented. This potential difference could affect the formation of the channel and, consequently, change the value of the threshold voltage. For the BGTC configuration, two possible vertical orientations are shown. In orientation a) the positive charge of the dipole points to the semiconductor and in b) it points to the dielectric. As pentacene is a p-type semi-

conductor, the channel must be formed by holes, which probably means that orientation a) will make it more difficult to form the channel and more threshold voltage will be needed (in absolute value). On the contrary, orientation b) will make more favorable the formation of the p-channel and less threshold voltage will be needed.

## II. EXPERIMENTAL PROCEDURE

Organic materials were deposited onto the crystalline silicon substrate by thermal sublimation under high vacuum conditions ( $10^{-6}$ mbar). The desired thickness layer was obtained by choosing the right exposition time (deposition rate was kept constant by temperature regulation). Metallic contacts were deposited in another vacuum chamber, where gold was also sublimated. This procedure was done to obtain both drain and source electrodes, which were defined by placing a metallic shadow mask over the sample. Resulting sizes of the channel are length (L) and width (W) of 80 $\mu$m and 2 mm, respectively. In relation to the gate electrode, it has been added manually afterwards using silver paint.

The fabricated OTFTs were characterized in a cryostat. Characterization was done in the dark and under vacuum conditions ($10^{-1}$ mbar). Electric current was measured by using a Keithley 2636A source meter. The output (drain current ($I_D$) versus drain voltage ($V_{DS}$)), transfer (drain current ($I_D$) versus gate voltage ($V_{GS}$)) and saturation (drain current ($I_D$) versus gate voltage ($V_{GS}$)) were obtained for every transistor. Last one is measured when $V_{GS}$ it is set equal to $V_{DS}$, what guarantees that the transistor is working in saturation regime.

## III. RESULTS & DISCUSSION

The effects of the glycine layer in OTFTs are studied by comparing the characteristics of every pair of transistors manufactured. FIG. 2, FIG. 3 and FIG. 4 stand for output, transfer and saturation characteristics of the 20 nm glycine layer in a BGTC configuration.

When comparing the output characteristics of both transistors (with and without glycine) in FIG. 2, it is remarkable to note that current is always higher, in absolute terms, in the one with the amino acid layer (except for the $V_{GS} = -30$ V case). Both of them present a clear linear and saturation regime for low and high drain voltages respectively, and cross the x axis at almost $V_{DS} = 0$ V.

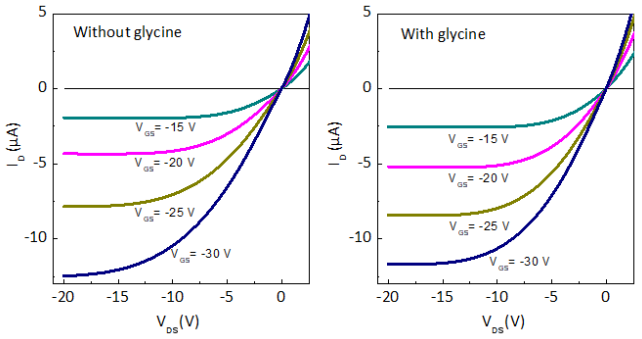


FIG. 2: Output characteristics (Left: OTFT without glycine layer. Right: OTFT with 20 nm glycine layer.)

Regarding transfer characteristics presented in FIG. 3, it is important to point out that current intensities for the same $V_{GS}$ voltage for the transistor with glycine present a considerable displacement towards more negative gate voltages $V_{GS}$ with respect to the one without the amino acid layer. This indicates that a higher voltage between gate and source is required to form a channel in the OTFT semiconductor layer and, thus, the threshold voltage will be higher for the OTFT with glycine. Moreover, both transfer characteristics show clearly an OFF and ON state, with an $I_{ON}/I_{OFF}$ ratio of around $10^7$ in both cases, although for the OTFT with glycine is a bit higher.

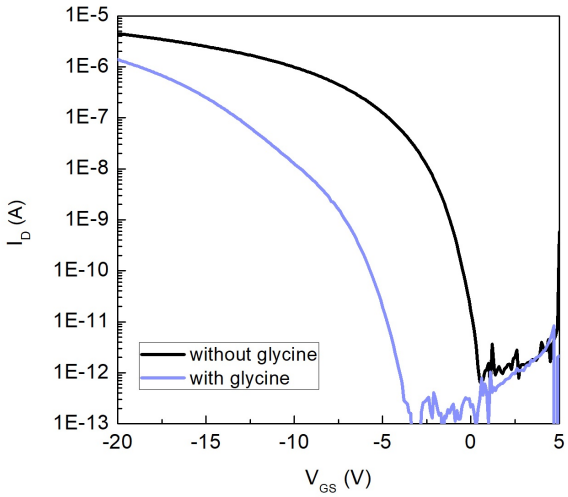


FIG. 3: Transfer characteristics ($V_{DS} = -5$ V) of the OTFTs without and with a 20 nm glycine layer

FIG. 4 shows the square root of the absolute value for the drain current as a function of $V_{GS}$. The drain current ($I_D$) for a TFT (as well as an OTFT), while in saturation regime, is analytically modeled as:

$$I_D = \frac{1}{2}\mu C_{ox}\frac{W}{L}(V_{GS} - V_{th})^2 \qquad (1)$$

Where $C_{ox}$ is the silicon dioxide capacitance and $W$ and $L$ are the width and length of the channel, respectively. $C_{ox}$ can be calculated from $C_{ox} = \epsilon_{ox}/t_{ox}$, where $\epsilon_{ox} = 3.9\epsilon_0$ and $t_{ox}$ is the thickness of the oxid.

Mobility ($\mu$) and threshold voltage ($V_{th}$) can be obtained from (1) as follows:

$$\mu = 2\frac{1}{C_{ox}}\frac{L}{W}\left(\frac{\partial\sqrt{I_D}}{\partial V_{GS}}\right)^2 \tag{2}$$

$$V_{th} = -\sqrt{I_D}\Big|_{V_{GS}=0}\left(\frac{\partial\sqrt{I_D}}{\partial V_{GS}}\right)^{-1} \tag{3}$$

It is convenient to mention that, taking into account these formulas, one would expect just a single slope in the saturation characteristic. However, devices show a non-ideal behaviour as reflected by the existence of a double slope, one for high values of voltage and other for smaller ones. The existence of a double slope has been reported several times [3,4]. In order to compute the mobility and the threshold voltage, only the slope for high voltages plotted in FIG. 4 has been considered.

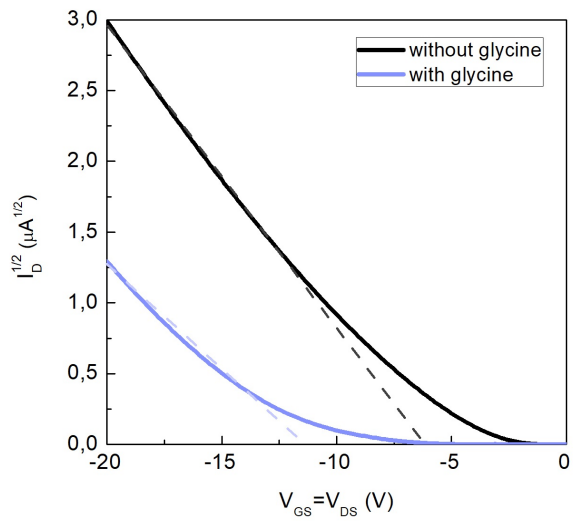


FIG. 4: Saturation characteristics of the OTFTs without and with a 20 nm glycine layer

The transistor without glycine presented a mobility of $\mu = 1.4 \cdot 10^{-1}$ $\frac{\text{cm}^2}{\text{Vs}}$ and a threshold voltage of $V_{th} = -6.4$ V, while the transistor with a 20 nm glycine layer showed a mobility of $\mu = 6.4 \cdot 10^{-2}$ $\frac{\text{cm}^2}{\text{Vs}}$ and a threshold voltage of $V_{th} = -11.4$ V. It is clear from these results that the addition of the glycine layer increases threshold voltage, (making a difference of 5 V), but lowers carrier mobility.

OTFTs with a 5 nm layer of glycine presented a threshold voltage of $V_{th} = -8.5$ V, that is between those of the transistor without glycine and the one with a 20 nm layer. This could be indicative of a relation between the thickness of the amino acid layer and threshold voltage shift.

BGBC transistors were tested as well, both with and without glycine. However, they did not provide any conclusive results regarding threshold voltage shifting. Mobilities were observed to be a couple orders of magnitude lower in the case of glycine though.

Results for 20 nm of glycine show a clear shift in threshold voltage. When a glycine layer is present, threshold voltage is higher, so that a larger voltage difference must be applied on the gate. A possible explanation for this phenomena would be that glycine molecules are vertically oriented with the positive charge upwards as suggested previously. In this way, holes are repelled in the pentacene layer upwards, meaning more voltage is required to form the holes channel at the bottom of it, thus explaining the increment of threshold voltage. It is important to note that in order to observe an effective difference all molecules should have the same vertical orientation or their effect would be cancelled. That would mean that its orientation might be determined due to chemical bonding with silicon dioxide and pentacene.

The effect of this dipole layer can also be studied from an alternative point of view, proposed by professor Supriyo Datta [5]. According to his model, current flows due to an electrochemical potential difference between drain and source electrodes and due to available electronic states in the semiconductor. The electrochemical potential might also be referred as to Fermi level or work function, and it is defined as the minimum energy to extract an electron at zero Kelvin.

Drain and source contacts are made of the same material (gold) so in absence of an external applied voltage, their electrochemical potential will be the same and no current will flow. If a voltage difference $V_{DS}$ between drain and source is applied, energy of the positive terminal is lowered by $qV_{DS}$ with respect to the other one and a current appears. It should be noted that holes flow from a lower potential to a higher potential. If $V_{DS} < 0$ then $I_D < 0$, which fits with experimental results.

Nevertheless, current can only occur if there are available states in the semiconductor, so that density of states and Fermi distribution must be taken into account. In order to make easier the comprehension of how $V_{GS}$ affects to the channel and the physical meaning of the threshold voltage, the following figure is shown:

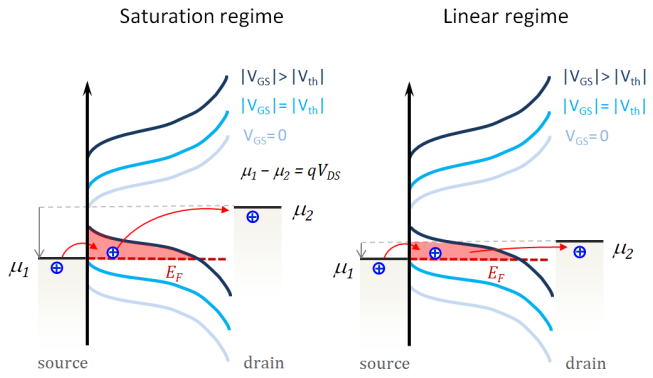


FIG. 5: Schematic diagram of the model proposed by Supriyo Datta. Horizontal axis: number of electronic states available. Vertical axis: energy. (Right: Linear regime model. Left: Saturation regime model.)

In FIG. 5 the vertical axis represents the energy and the horizontal axis is the number of states, which is the product between the fermi distribution and the density of states. Notice that available states are those which reside between the drain energy ($\mu_2$) and the source energy ($\mu_1$), painted in red in the figure. As $V_{DS}$ and $V_{GS}$ are measured respect the source, $\mu_1$ is taken as the reference level.

The function of $V_{GS}$ is to shift the curves of the available states up and down. Firstly, consider that $V_{GS}$ is zero, in this case, as shown in the figure, there are no available states, as the source and drain energy interval falls in the energy gap of the semiconductor. If a negative $V_{GS}$ is applied, the curve is shifted upwards. While making $V_{GS}$ more negative, there is a point at which the higher point of the curve of the valence band coincides with $\mu_1$; that is, at this point available states start to appear. The $V_{GS}$ needed to arrive to this point is the threshold voltage, $V_{th}$: as there are available states in the semiconductor, the channel starts to be formed and holes can flow through it. If $V_{DS}$ remains fixed and $V_{GS}$ continues being more negative, more states are available and the current becomes higher.

Given a $V_{GS}$ more negative than $V_{th}$, if $V_{DS}$ is varied $\mu_2$ changes and, consequently, the number of states also changes. It is interesting to point out that two different cases can be considered: linear and saturation regime. In linear regime, if $V_{DS}$ is more negative, $\mu_2$ is higher and more states are available in the channel, increasing the current that flows through it. This does not happen in saturation regime. In saturation regime a $V_{DS}$ is applied such that $\mu_2$ surpasses the maximum of the valence band curve. Even though $\mu_2$ continues to increase, the number of states remains equal, as now $\mu_2$ is on the gap energy region and no more states are added.

Taking into account the results obtained, the effect produced by a glycine layer is probably the presence of a permanent positive difference voltage through it. As a consequence, the number of states curves are shifted down, meaning that $V_{GS}$ must be more negative in order to have a channel formed or, in other words, the absolute value of $V_{th}$ must be higher. Actually, this also agrees with the idea that the positive charge of the amino acid dipoles points upwards.

## IV. CONCLUSIONS

The aim of this project was to study the effect of a glycine layer on OTFTs. OTFTs with a glycine layer have been successfully manufactured and characterized. Moreover, effects of the glycine layer have been observed: the addition of a dipole layer results in a change of the threshold voltage mainly. In particular, absolute value of threshold voltage increases when a glycine layer is added. A 5 V difference in threshold voltage was observed in a BGTC organic transistor with a glycine layer of 20 nm thickness. Smaller differences have also been noted in current and mobility but a satisfactory explanation has not been found yet. A plausible hypothesis would be that the dipole layer affects the morphology of the organic semiconductor above. This phenomenon is already being studied in the case of self-assembled monolayers (SAMs).

More measures should be done in order to confirm the apparent relation between the dipole layer thickness and the shift experienced by the threshold voltage. Also how glycine bonds to pentacene and $SiO_2$ should be studied in detail. Knowing the nature of the bonding would give valuable information to complete the understanding of the observed phenomena.

Furthermore, other amino acids with different dipolar moment could be implemented. It is expected that the higher the dipole moment, the larger the shift in the threshold voltage. If this correlation was true, it might be possible to determine which amino acid forms the dipole layer.

In conclusion, first results show a promising line of investigation. More research should be done on the topic and further results might give rise to future applications.

## V. ACKNOWLEDGEMENTS

We greatly thank Joaquim Puigdollers for his guidance and supervision in this project.

## VI. REFERENCES


[1] Cheng Huang, Howard E. Katz, and James E. West. *Solution-Processed Organic Field-Effect Transistors and Unipolar Inverters Using Self-Assembled Interface Dipoles on Gate Dielectrics.* Langmuir. 2007. Vol. 23: issue 26. Pages 13223-13231.

[2] Mahdieh Aghamohammadi,Reinhold Rödel,Ute Zschieschang, Carmen Ocal, Hans Boschker, R. Thomas Weitz, Esther Barrena, and Hagen Klauk. *Threshold-Voltage Shifts in Organic Transistors Due to Self-Assembled Monolayers at the Dielectric: Evidence for Electronic Coupling and Dipolar Effects.* American Chemical Society, Applied Materials and Interfaces. 2015. Vol. 7: issue 41. Pages 22775-22785.

[3] Hung Phan, Michael J. Ford, Alexander T. Lill, Ming Wang, Guillermo C. Bazan, and Thuc-Quyen Nguyen. *Electrical Double-Slope Nonideality in Organic Field-Effect Transistors.* Advanced Functional Materials. 2018. Vol. 28: issue 17. Pages 1707221.

[4] Marta Reig, Gintautas Bagdziunas, Arunas Ramanavicius, Joaquim Puigdollers and Dolores Velasco. *Interface engineering and solid-state organization for triindole- based p-type Organic Thin-Film Transistors.* 2018. *Submitted.*

[5] Supriyo, Datta. *Lessons from Nanoelectronics. A New Perspective on Transport.* Chapter I.2 Why electrons flow. Singapore. 2012. Pages 15-24.