Organic semiconductors and Transistors: state-of-the art Review

Essam Abu-ElMkarem, 18011055, Khaled Gehad Hamed, 18010592, Armia Khairy Fahmy, 18010293, Mohamed Ezzat Fayek, 18011553, Nada Abdo Hanafy, 18011976, Alaa Ahmed Abu-Bakr, 18010370

***Abstract*—This paper reviews the Organic Semiconductors and theory behind its development and a brief of the history. around developing this technology. A lot of it will discuss the distribution of energy bands in organic semiconductors and the optical properties and luminescence effect when some organic materials such as Phthalocyanine and Polymers such as poly-para-phenylene-vinylene. and will discuss OFET and applications of Optical Amplifiers.**

***Index Terms*—organic semiconductors, Phthalocyanine, Polymers, poly-para-phenylene-vinylene, OFET, etc.**

I. INTRODUCTION

THE major event that marked the birth of organic semi-conductors is most probably the unveiling of conducting polymers in 1977 . It was actually at this time that it became possible to envision the use of organic materials for the fabrication of devices in which an electrical signal is modulated. Although they have been identified as early as 1948, organic semiconductors have not been used in practical devices until the middle of the 1980's During fifteen years, electronic organics remained a confidential field of research where only a small handful of academic teams were involved. Since the outset of the 21st century, it has experienced a tremendous development in both academic and industrial institutions. Up to now, this growth was mainly related to the organic light-emitting diodes, with the advent of several commercial devices as early as 1999.

In the inorganic semiconductors such as Si and Ge, the atoms are held together with very strong covalent bonds, as high as 300 kJ/mol for Si. In these semiconductors, charge carriers move as highly delocalized plane waves in wide bands and indicate a high mobility of charge carriers ¿¿ 1 cm2/Vs. In organic semiconductors, intramolecular interactions are also mainly covalent, while intermolecular interactions are usually induced by much weaker van der Waals and London forces resulting in energies smaller than 40 kJ/mol. Thus, the transport bands in organic crystals are much narrower than those of inorganic ones, and the band structure is easily broken by disorders in such systems, leading to creation of states in the energy gap.

Almost all organic solids are insulators. However, in organic crystals that consist of molecules that have the conjugate system, electrons can move via electron cloud overlaps. That is why these crystals exhibit electrical conductivity. Polycyclic hydrocarbons and phthalocyanine salt crystals are examples of this type of organic semiconductor. Among the conjugated polymers there exist conductive and semi-conductive polymers.

II. ORGANIC SEMICONDUCTORS

Organic semiconductors are organic solids made of conjugated molecules characterized by an alternation between singly and doubly bound carbon atoms. In these unsaturated molecules, the presence of pi-orbitals offers the availability of electrons that can involve in charge transport mechanisms. In the beginning, conducting polymers were seen as potential substitutes for metals with the major advantages of light weight and easy processing. Actually, the serendipitous discovery of electrically driven light emission in poly-para-phenylene-vinylene (PPV) moved the interest of conducting polymers to organic electronic devices. The family of organic conjugated materials comprises several conjugated polymers, but also short molecules that can be either oligomers (short polymers with a well-defined number of monomers in their backbone) or specific molecules like phthalocyanines.

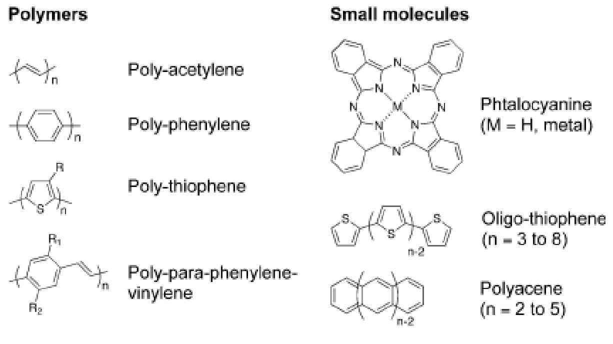


Fig. 1. Illustrating Polymers and small molecules

III. OPTICAL PROPERTIES

In the last two decades, organic semiconductors have been intensively studied as novel materials for optoelectronics. They combine the simple processing of plastics with electronic function and efficient light emission. They have been applied across the spectrum of optoelectronic devices, including organic light-emitting diodes (OLEDs) photovoltaics, transistors, optical amplifiers, and lasers. Their unique combination of properties has enabled new device geometries and processing techniques, leading, for example, to printable optoelectronics. The main research focus has been on OLEDs for light-emitting displays; these are now commercially available, and their considerable success makes the wider study of the use of these materials for other light-emitting devices a promising field of study.

Organic semiconductors are particularly appealing as novel laser gain media . They have four-level energy systems in which vibrational and structural relaxations separate the absorption and emission bands. Strong optical transitions (peak absorbance of 105 cm-1 and emission cross-section 10-16 cm2) give the potential for large optical gain in very compact devices. Like conventional laser dyes, organic semiconductors are broadband emitters; and, through simple changes in chemical structure, the emission may be tuned across the visible spectrum. However, unlike conventional dyes, they show little concentration quenching and can have fluorescence quantum efficiencies greater than 90% in undiluted films. Consequently, organic semiconductors are very well suited for compact tunable lasers and broadband optical amplifiers.

All organic semiconductor lasers and optical amplifiers are currently optically pumped, meaning that another light source is needed to excite the organic semiconductor. There has been good progress in developing miniature systems, and pulsed microchip lasers are now routinely used to drive broadly tunable organic distributed feedback lasers. There also have been several demonstrations of organic semiconductor lasers pumped by nitride diode lasers, and even an LED-pumped polymer laser. Furthermore, the semiconducting properties of these materials give a prospect in the longer term for electrically pumped organic semiconductor lasers and amplifiers.

In organic semiconductors, like their inorganic counterparts, the semiconducting properties arise from the overlap of atomic orbitals. In conjugated molecules (those that have alternating single and double bonds), three of the four valence electrons of carbon typically make covalent -bonds with neighboring atoms in the plane of the molecule. The fourth electron is in a Pz orbital, which is oriented perpendicular to the plane of the molecule. Overlap of these orbitals leads to covalent -bonding and electron delocalization along the molecule, as illustrated in Fig. and this in turn leads to semiconducting electronic properties. Molecular orbitals formed of Pz atomic orbitals can be bonding ()or anti-bonding (*). Usually, the highest occupied molecular orbital (HOMO) has two electrons in the bonding -orbital. One of these can be excited to the lowest unoccupied molecular orbital (LUMO), which is an antibonding *-orbital. Optical transitions between HOMO and LUMO determine the lowest energy absorption and luminescence properties in organic materials. Hole transport occurs by hopping between HOMOs of neighboring molecules, whereas transport of electrons is by hopping between the LUMOs of neighboring molecules. While the HOMO and LUMO are analogous to the valence and conduction bands of inorganic semiconductors, it is only in the most ordered organic semiconductors that band-like transport is possible. Most organic semiconductors are much more disordered than inorganic semiconductors leading to hopping transport.

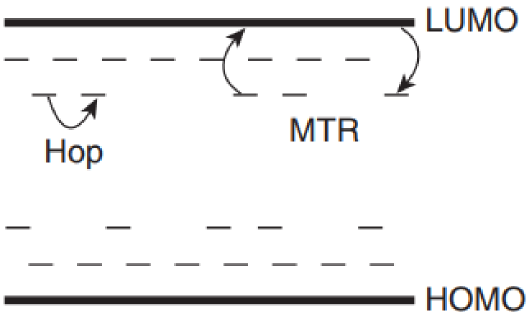


Fig. 2. Illustrating Hoping transport

Hopping transport is a site-to-site phonon-assisted thermally activated tunnelling mechanism between localized bandgap states that are spatially and energetically close , classically described by Vissenberg and Matters. In a charge transport model based on variable range hopping, localized charge carriers in amorphous organic films are not activated to a transport level, but instead are able to hop directly from site to site, either a short distance where there is high activation energy or a long distance where there is low activation energy. The model predicts that μ0 will increase with increasing gate voltage. This can be explained qualitatively by assuming that accumulated charge carriers will fill lower-lying energy states first. As the lower energy traps are filled, it becomes less likely that other mobile charge carriers will become trapped, so trapping becomes less efficient and μ0 rises. Subsequent charge carriers will occupy states with higher energies requiring less energy to hop between sites. Mobility μ0 also increases with temperature and is strongly dependent on the density of localized states.

Another model for (polycrystalline) organic materials is the MTR model. In this transport model, the semiconductor consists of crystallites separated by grain boundaries. This model differs from hopping models in that it predicts that 9 Organic Semiconductors charges will move in delocalized bands within crystallites until they are trapped at the grain boundaries. These traps may be caused by impurities or physical defects. Charge carriers fall into a trap of localized states in the bandgap and remain trapped until they are released by thermal activation to a transport level, whereupon they once again become active. The time spent in the trap depends on the temperature and on the depth of the trap.

Organic laser dyes are also conjugated molecules, which can give optical gain upon optical excitation in solution or when dispersed in an inert matrix. The advantages of conjugated polymers are that they can have high photoluminescence quantum yields even as neat films, thereby enabling very high optical gain in solid state; their scope for simple fabrication of waveguides; and the future prospect of electrical pumping, such as seen in this figure.

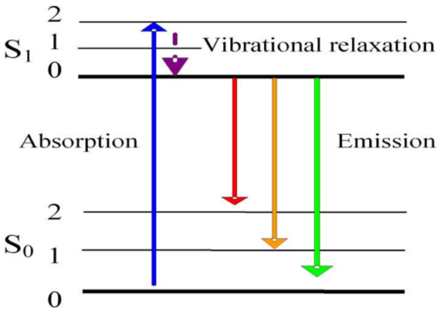


Fig. 3. Illustrating Absorption and Emission of energy

A photon of energy equal to or greater than the difference in energy between the HOMO and LUMO can be absorbed by the material and will excite a molecule from the ground state S0 to a singlet excited state. The lowest singlet excited state is called S1, and higher lying singlets are S2, S3, etc. Each electronic state has many vibrational(Energy) levels (indicated as 0, 1, and 2 in Fig. 2 . Before absorption of the photon, almost all molecules are in the zero vibrational level of the S0 state because the spacing between vibrational levels is much larger than a thermal energy. Absorption occurs to one of the vibrational energy levels of the singlet excited state depending on photon energy. Following absorption, relaxation to the zero vibrational energy level of S1 state occurs predominantly within 1 picosecond . Photon emission (spontaneous or stimulated by an external photon) occurs from the lowest vibrational level of the S1 state to each of the vibrational levels of the ground state S0.

IV. ENERGY BANDS

In chemistry, HOMO and LUMO are types of molecular orbitals. The acronyms stand for highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively. The HUMO is equivalent to the maximum of the Valence Band, and LOMO is equivalent to the minimum of Conduction Band.

The shape of the energy bands appearing in organic semiconductor devices, especially at the contact area, is essential in understanding the transport processes in a particular device. Almost all OFETs have the structure with low work function electron and high work function hole injecting source/drain contacts to a conjugated polymer organic semiconductor.

V. ORGANIC SEMICONDUCTOR MATERIAL TYPES

The mobilities of organic semiconductors have achieved significant progress in OFETs from the initially reported 10 -5 cm2/V.s for polythiophene in 1986 to 10 cm2/V.s for 132 Different Types of Field-Effect Transistors - Theory and Applications present diketopyrrolopyrrole (DPP)-based polymers . The high mobility of organic semiconductors over conventional amorphous silicon indicates large potential application of organic electronic devices. The remarkable progress of organic semiconductors provides a road for organic electronic industry. Generally, for high-performance organic semiconductors, some critical factors, such as molecular structure, molecular packing, electronic structure, energy alignment, and purity, play important roles. Among them, tuning the molecular packing is especially important for high-performance semiconductors since the charge carrier transport is along the molecular π-orbitals. Hence, the overlap degree of neighboring molecular orbitals significantly determines the charge carrier mobility. Molecular packing with strong intermolecular interactions is favorable for efficient charge transport and high field-effect mobility. The electronic structure and energy levels are crucial for the materials and device stability. In order to obtain the high-performance and stable organic semiconductors, structural modification with electron donors and acceptors are necessary. Except the above talked aspects, the film morphologies such as grain boundaries also could affect the charge carrier transport. The grain boundaries and disordered domains could hamper the efficient intermolecular charge hopping between them. Hence, increasing the crystal grain size and film uniformity could efficiently improve the charge transport and mobility. In this section, we introduce some feature compounds with mobility of/over amorphous silicon and/or with high stability.

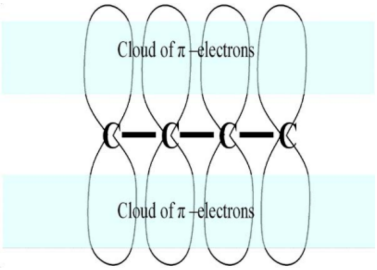


Fig. 4. Illustrating cload of π elelctron

In the last two decades, p-type semiconductor materials have achieved much progress because of their simple design and synthetic approach. P-type organic semiconductors mainly contain acene, heteroarene, thiophenes, as well as their correlated oligomers and polymers, and two dimensional (2D) disk-like molecules. Several comprehensive reviews have given detailed information about these compounds. Among them, the polycyclic aromatic hydrocarbons are most representative of the class of compounds due to their unique features. Some representative p-type semiconductors are shown in Chart 1. Pentacene, as the benchmark of organic semiconductors, was first reported in 1970s, but the numerous OFET applications were only conducted recently. With strong intermolecular interactions and herringbone packing motif, pentacene exhibits efficient charge transport. Hence, polycrystalline thin film of pentacene and tetracene showed surprisingly high mobility approaching 0.1 cm2/V.s, and 3.0 cm2/V.s, respectively. The substituted tetracene derivative rubrene showed the highest charge carriers' mobility with 20 cm2/V.s for single crystal device in the FET configuration. This implies that the conjugated acene is a good building block for the p-type semiconductors. Later on, phthalocyanines and more core-extended hexa-peri-benzocoronenes (HBC) containing two-dimensional (2D) aromatic core were reported and showed typically discotic columnar liquid crystalline phases. As a result, the HBC showed enhanced mobility along the column due to the solid-state organization. Moreover, HBC-based OFETs by zone casting method exhibited a high mobility up to 0.01 cm2/ V.s. The chemistry based on acene has paved the way for designing efficient p-type semiconducting materials.

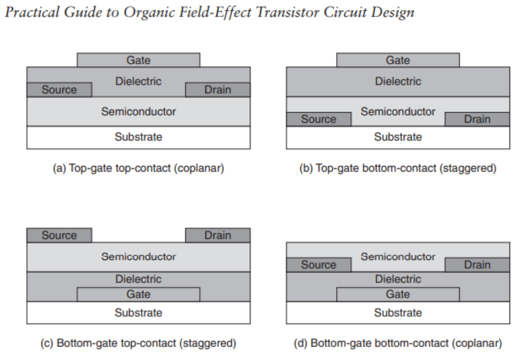
Although the p-type semiconductor materials have achieved much progress, the development of n-type organic semiconductors still lags behind that of p-type organic semiconductors due to low device performance, ambient instability, and complex synthesis. Owing to their important roles in organic electronics, such as p-n junctions, bipolar transistors, and complementary circuits, it is desirable to develop stable n-type semiconductor materials with high charge carrier mobility for organic field-effect transistors. To date, n-type organic semiconductors with high mobility are relatively rare and significantly lagging behind p-type semiconductors, and most of the n-type materials are still air unstable in ambient conditions due to its high lowest unoccupied molecular orbital (LUMO) energy level. reasoned that the air unstable problem is due to redox reaction with oxygen and water. Based on this result, we can calculate the LUMO energy level, and it should be lower than -3.97 eV in order to be stable toward water and oxygen. N-type organic semiconductors mainly contain halogen or cyano-substituted n-type semiconductors that could be converted from p-type materials, perylene derivatives, naphthalene derivatives, fullerene-based materials, and so on.

VI. FIELD-EFFECT TRANSISTORS

An organic field-effect transistor (OFET) is a three-terminal device – gate, source, and drain – where, conventionally, the conductivity of the device is controlled by a vertical electric field from the gate terminal acting upon a horizontal conduction channel that has been formed in the semiconductor between the source and drain electrodes.

An organic thin-film transistor (OTFT) is a special case of an OFET in which the semiconductor and dielectric are deposited as thin films on top of an inactive substrate that plays no part in the transistor behavior.

There are four possible configurations of gate, source, and drain in an OTFT . The most popular configurations are the bottom-gate bottom-contact architecture, for its ease of fabrication in research labs, and the top-gate bottom-contact architecture, which offers the largest area for charge injection and extraction. There is a further classification of staggered or coplanar device, depending on the charge carrier path within the gate-induced accumulation channel. The current path within a coplanar configuration is almost entirely horizontal, whereas in a staggered configuration the current path is vertical near the source and drain, which offers a larger area for charge injection into the semiconductor. Transistors are primarily described by their conduction channels: p-type transistors are those with hole-accumulated channels, while n-type transistors are those that operate with electron-accumulated channels. For p-type transistors, as holes are the charge carriers, the source is the most positive terminal, and is often made of a high-work-function metal such as gold (5.1 eV). Conversely, for n-type transistors, electrons are injected from the negative source terminal, which is ideally a low-work-function metal such as calcium (2.9 eV), though these may not be environmentally stable.



(a) Top-gate top-contact (coplanar) (b) Top-gate bottom-contact (staggered)

(c) Bottom-gate top-contact (staggered) (d) Bottom-gate bottom-contact (coplanar)

Fig. 5. Illustrating organic field-effect transistor circuit

It is convenient to reference all transistor voltages to the source electrode. In this respect, a drain-source voltage (VDS) and a gate-source voltage (VGS) are applied. The application of VGS modulates an electric field across the transistor channel, which causes an accumulation of charge carriers at the semiconductor–dielectric interface. The depth of the conducting layer is very thin, no more than a few nanometers at the surface of the semiconductor at the interface.

VII. TRANSISTOR OPERATION

When a gate voltage is applied, a field is induced at the semiconductor–insulator interface that causes the highest occupied molecular orbit and lowest unoccupied molecular orbit to shift relative to the source and drain Fermi levels which are held at a fixed value by external voltages. If the gate voltage is large enough, mobile charge carriers will flow from the source contact into the semiconductor. When a potential difference is then applied to the source–drain, charge carriers will flow to the drain contact, completing the electrical circuit.

1-In the off state, VGS $<<$ VT, there is no accumulated conducting channel. The source– drain current, IDS, is very small and is determined by the intrinsic conductivity of the bulk semiconductor:

$$I_{DS(cut-off)} = I_{leak} \text{ when } V_{GS} << V_T$$

Fig. 6. where I(leak) is a small intrinsic leakage current in the bulk semiconductor and VT is the threshold voltage.

2- In the subthreshold region, VGS < VT the source–drain current, IDS, increases exponentially with gate voltage, similarly to the current due to a forward-biased diode. This exponential behavior is often attributed to deep trap states.

$$I_{DS(subthreshold)} = I_{S0} e^{\frac{V_{GS}}{nV_{th}}} \text{ when } V_{GS} \le V_T$$

Fig. 7. where Vth = kT/q is the thermal voltage (26 mV at room temperature), n is the subthreshold slope factor, and IS0 is a process-dependent parameter that also has some dependence on VT. These two parameters, IS0 and VT, are best extracted from experimental data.

owing to the large values of VT, subthreshold behavior is important and accounts for a significant amount of current. This current is often considered to be a parasitic leakage current in digital circuits, but in analogue circuits it may be utilized very efficiently in a similar manner to BJT devices or low-power metal-oxide semiconductor field-effect 20 Practical Guide to Organic Field-Effect Transistor Circuit Design transistor (MOSFET) devices. Performance of a device in the subthreshold region is measured by the subthreshold slope parameter n, which is defined as the change in VGS needed to effect a decade increase in IDS current.

3-in the linear region, VGS VT and VDS ¡ VGS VT. A conducting channel at the semiconductor–dielectric interface is only formed when VGS is greater than the VT. An equal amount of charge, but opposite in sign, appears on either side of the dielectric. The VT is the result of either shallow traps in the semiconductor, which need to be filled, or charged dipoles already in the channel, which need additional gate voltage to form the channel

$$I_{DS(linear)} = \frac{W}{L}\mu C_{diel}\left[(V_{GS}-V_T)V_{DS}-\frac{1}{2}V_{DS}^2\right] \text{ when } V_{DS} < V_{GS}-V_T$$

Fig. 8. where μ is the surface mobility of the channel, Cdiel is the capacitance per unit area of the gate dielectric, W is the channel width, and L is the channel length.

Saturation occurs when VGS $\leq$ VT and VDS $\leq$ VGS$-$VT. At these terminal voltages, the potential at some point in the channel drops to zero. At this position in the channel, approximately where VGS < VDS, there is now no longer an effective VGS to maintain the charge in the channel. A region depleted of charge carriers forms next to the drain, and the channel is pinched off, with the source–drain current saturated. Further increases in VDS will widen the depletion region next to the drain and move the pinch-off point towards the source, resulting in a shorter accumulated channel length, less resistance, and a small increase in IDS. IDS is now substantially independent of VDS and is mainly controlled by VGS. By substituting VDS = VGS VT in Equation:

$$I_{DS(linear)} = \frac{W}{L}\mu C_{diel}\left[(V_{GS}-V_T)V_{DS}-\frac{1}{2}V_{DS}^2\right] \text{ when } V_{DS} < V_{GS}-V_T$$

and adding a parameter for the channel length modulation, the source–drain current for the saturation region can be derived:

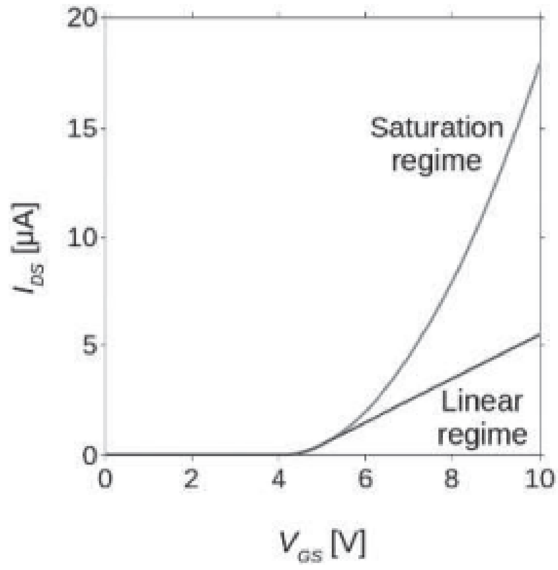
$$I_{DS(sat)} = \frac{1}{2}\frac{W}{L}\mu C_{diel}(V_{GS}-V_T)^2(1+\lambda V_{DS}) \text{ when } V_{DS} < V_{GS}-V_T$$

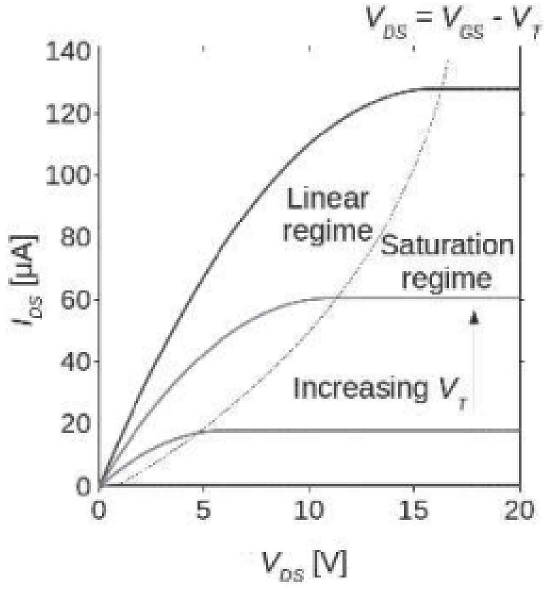
Fig. 9. where λ is the channel length modulation parameter.

a transistor gain factor, β, may be defined

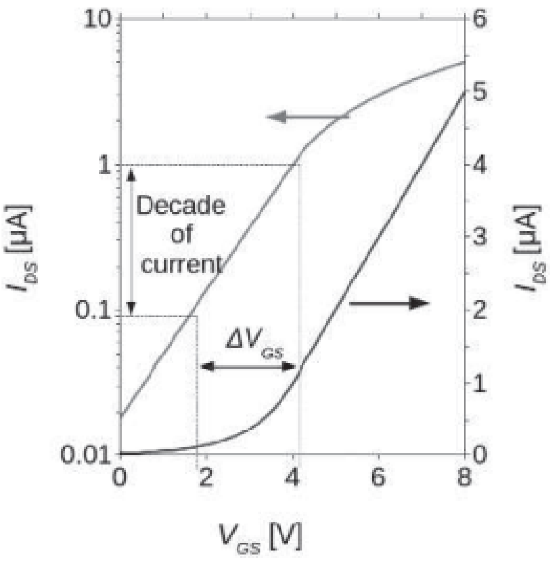
$$\beta = (\mu C_{diel})\frac{W}{L} = \left(\mu\frac{\epsilon_r\epsilon_0}{d_{diel}}\right)\frac{W}{L}$$

Linear and saturation transistor regions of operation output curves





The sub-threshold transfer characteristic



VIII. Conclusion

Organic Transistors and Semiconductors are still in rapid researching and development since it's such a complicated mission to describe and study the operations of multiple structures of organic materials and a very vast variety and number of organic materials in which may include ones that can be a revolutionary potential to new devices and discoveries or lead to it, Despite that, research and development in this field yielded many devices and applications such as OLED Panels in manufacturing Monitors of various sizes and shapes, and powerful LASERs for Projectors and scientific research, and Optical Amplifiers, which is what made Fiber Optics communications over vast distances viable, and Modern transistors such as OFET and Thin-FET (TFT), where the development on it led into making Transistor logic design on thin and flexible sheets of plastic, which can be embedded into clothes and wearables and any thin accessories. Most recent is ARM making a plastic model of its ARM-Cortex-M0 CPU, despite it consumes more energy than the equivalent crystalline silicon-based CPU, they have lower manufacturing costs than them. This opens a new era for develop and construct the future and may change it to unprecedented leaps in technology as we know it.

References

[1] M.J. MALACHOWSK and J. ZMIJA, *Organic field effect transistors*. Institute of Technical Physics, Military University of Technology, 2 Kaliskiego Str., 00908 Warsaw, Poland

[2] G. Horowitz, *The organic transistor: state-of-the art and outlook*. University Paris Diderot, 15 rue Jean-Antoine de Baif,75205 Paris, France

[3] D. Elkington, N. Cooling, W. Belcher, P.C.Dastoor and X. Zhou, *Organic Thin-Film Transistor (OTFT)-Based Sensors*. Centre For Organic Transisitor,Physics,The University of Newcastle,Callaghan,NSW 2308,Australia

[4] A. Sou, *Practical Guide to Organic Field-Effect Transistor Circuit*. Smithers Rapra Technology (April 18, 2016)

[5] W. Brutting, *Physics Of Organic Semiconductors*. WILEY-VCH Verlag GmbH Co. KGaA

[6]Ortstein, K., Hutsch, S., Hambsch, M. et al. *Band gap engineering in blended organic semiconductor films based on dielectric interactions*. Nat. Mater. 20, 1407–1413 (2021).