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3

Organic Semiconductor Based Heterostructures for Optoelectronic Devices

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1. Introduction

In the last decades organic materials are considered a very important alternative to the inorganic semiconductors in the manufacturing of a large variety of devices because of the great diversity of the organic compounds, their remarkable properties, low production cost, compatibility and complementarity with the very well known silicon technology. Lately the organic semiconductors started to represent a new class of materials very attractive for opto-electronic applications (Huang, 2002; Tang, 1988; Forrest, 2000; Kalinowski, 2003) and electronic applications (Dodabalapur, 1995; Karl, 2000; Katz, 2000 a; Horowitz, 1999; Torsi, 2000; Schön, 2000 a; Inoue, 2005) in particular light emitting devices and lighting sources (Yersin, 2007; Van Slyke, 1996; Wang, 2005; Dini, 2005), solar cells (Lane, 2005; Ameri, 2009; Troshin, 2008; Duggal, 2005), photodetectors (Hofmann, 2005; Troshin, 2008), field effect transistors (Molinari, 2007; Mas-Torrent, 2008) and lasers (Duarte, 2009; Liu, 2009) being considered candidates to replace the inorganic semiconductors.

The electroluminescence (EL) of the organic molecules is a well-known phenomenon for more than 50 years, but only in the late '80th has become utile for practical applications. The successful application of the organic materials luminescence in Light Emitting Devices (OLEDs) requires adequate device structures to overcome the problems associated with the high resistivity of the organic materials and with the difficulty to obtain a good charge injection from the electrodes in the organic layers. These devices have a thin film architecture, which includes both organic/organic and organic/inorganic interfaces.

Starting with the first prototype of OLED (Vincett, 1982), lately has been proposed the first efficient OLED based on heterostructures containing thin films from small molecule organic compounds (Tang, 1988) that have shown an attractive efficiency (1% external quantum efficiency, 1.5 lm/W luminous efficiency, higher than 1000 cd/m^2 brightness) and driving voltage below 10 V.

From this moment, different types of OLEDs have been realised, based on both fluorescence and phosphorescence, that have started to be used in mobile, small dimension displays. Probably, the most spectacular application of the Organic Light Emitting Devices is in the flat panel displays for TV and monitor technology because they are characterized by high brightness and wide viewing angle, which are the most important advantages over the liquid crystals. Significant effort is devoted now to increase the quantum efficiency, lifetime and thermal stability of these devices. Devices with high efficiencies, low working voltages

and long lifetime involve low electrical resistivity and good chemical stability of the contact organic semiconductor/metal to assure a good charge carriers injection and transport. On the other hand the particularities of the charge injection and transport across the inorganic/organic and organic/organic heterojunctions are determinant for the properties of the devices. The improvement of the organic electroluminescent diode performances involves the separate optimisation of the two processes implied in the radiative emission phenomena: 1. the injection and transportation of the charge carriers and 2. their radiative recombination in different layers. The injection of the charge carriers must be not only efficient but also stable under operation conditions.
In this chapter we summarize some results of our work in the field of applied research concerning the charge injection and transport through inorganic/single and multilayer organic heterostructures.

2. OLED structure. General considerations

The basic p-n structure is formed from two organic thin layers, one a holes transporting layer (HTL) and the other an electrons transporting layer (ETL), which can be also the emitting layer where the recombination takes place. The organic layers are disposed between an anode and a cathode and are offering an adequate medium for the charge transfer through the interface situated between the two organic layers. In the OLED structures the relevant mechanism of electroluminescence involves several steps: injection, transport, capture and radiative recombination of the positive and negative charge carriers inside an organic semiconductor characterized by an energy band gap suitable for yielding visible light.

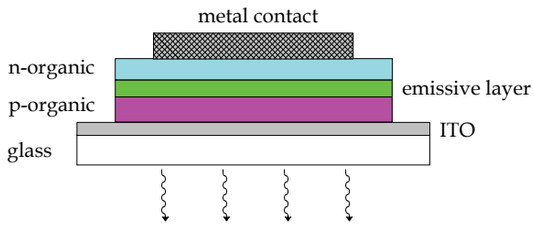


Fig. 2.1. Basic p-n junction for OLED application

The OLED structure is delimited by the metallic layer and the transparent conductor such as indium tin oxide (ITO)/glass interfaces. While the electrical properties are controlled by the mobility of the charge carriers and the energy levels offset between the layers that compose the heterostructure, the optical properties are controlled by the refractive index mismatches at the interfaces glass/air and organic layer/transparent conductor. These mismatches generate the trapping of a large fraction of the incident light by the total internal reflection into glass and transparent conductor (ITO) (Lu, 2002). An improved electroluminescence can be obtained by the individual optimization of the steps mentioned above (injection and recombination), in the configuration of organic multilayer light emitting devices based on hetero-interfaces between different organic materials.
Multiple layers can be used to increase the quantum efficiency or avoid the degradation of the devices. This way can be assured a balanced injection of the charge carriers. Since

recombination of the electrons and holes within an organic layer gives rise to luminescence, it is necessary that both charge carriers are simultaneously injected in equal numbers from both electrodes, in the organic layer. This can be achieved by the optimization of both electrons and holes transporting layers or by the use of intermediate organic layers acting as blocking layers that assure a good separation of the charge carriers.

The first critical factor in determining the OLED efficiency is the charge injection being correlated with the lifetime of the device. The electrodes are used to inject charge into or to extract charge from the organic semiconductor layers, more precisely to inject electrons and holes into opposite sides of the emissive organic layers: (1) the electrons are injected from the Fermi level of the cathode into the lowest unoccupied molecular orbital (LUMO) of the organic, overcoming the contact barrier; (2) the hole are injected from the Fermi level of the anode into the highest occupied molecular orbitals (HOMO) of the organic. To improve the carrier injection, the energy level for the charge carriers in organic should match the electrode work function. On the other hand the HTL and the ETL should be characterized by high mobility carriers to assure the transport of the injected carriers to the emission zone.

The second critical factor is the radiative recombination of the charge carriers in the bulk of the organic layer. The electrons and holes accumulated at the HTL and ETL interface are creating pairs, known as excitons, that release the energy as light. Beside the improvement in the fluorescence yield of the emitting material, which can be obtained by doping, a well-balanced injection of positive and negative charge carriers is necessary.

The inorganic semiconductor/organic and/or metal/organic junction, as the key element(s) of any organic device, can offer the possibility to overcome the disadvantages of the conventional inorganic heterostructures, but the process of injection of the charge carriers across the interfaces of the structure and the transport of the hole and electrons inside the structure influence the performances of the organic devices.

Other important processes dominating the electrical properties of the interfaces and affecting the performance and lifetime of the devices, are the diffusion and chemical reaction of the metal deeper into the organic layer at the metal/organic interface and the molecular interdiffusion at the organic/organic interface.

In some molecular compounds, the intermolecular coupling is supposed to be stronger because of the significant overlapping between the π electrons clouds supporting the charge carriers generation and transport, leading to a significant delocalization of electrons and, as a consequence, a relatively significant intrinsic conductivity.

The limitation in performance of the device realized with organic semiconductor characterized by low charge mobility ($\mu << 1$ cm^2/Vs) is determined by the current limitation due to the space charge. This process is favoured if one contact is able to inject more carriers than would be present in semiconductor at thermal equilibrium. The electrical transport properties are determined by the low mobility of the charge carriers in organic solids (2 or 3 orders of magnitude lower than in silicon) that induces a limitation associated with the space charge and by the grain boundaries, defects and imperfections in the organic films acting as trap centres that induce a limitation associated with the trap charge.

Another source for the generation of interfacial space charge in hetero or multilayer devices can be the energy level offset at the organic/organic interfaces. Even the energy barriers are not present, the differences in the charge carriers mobility between the layers can generate a mobility barrier at hetero-interfaces, which can also be a source for the generation of interfacial space charge. Trapped and interfacial charges have an important effect on the performances of the OLEDs (Riess, 2001).

A stronger emission can be obtained introducing a supplementary luminescent layer between the holes transporting layer and the electrons transporting layer, as it is presented in Figure 2.1, but this way the manufacturing of the OLED more is complicated.
If we use doping to improve the fluorescence, the electrical properties of the resulted "host-guest" material can be controlled through the selection of the dopant (Makinen, 2002). The electronic transfer direction and the doping polarity are strongly depending of the relative position between HOMO and LUMO for dopant (guest) and matrix (host) molecules. So, a good concordance between the ionisation energy (IE) corresponding to HOMO for the host matrix and the electron affinity (EA) corresponding to LUMO of the dopant molecule is necessary to produce a „p" type doping while the alignment between the LUMO level of the host matrix and the HOMO level of the dopant molecule leads to a „n" type doping. Fermi level will freely move inside the band gap HOMO-LUMO of the host matrix and dopant, supposing that this movement is not limited by the band edges (no pinning phenomenon).
The role of the dopants is very complex. On one hand the doping of the "p" and "n" transport layers has two important transport effects: 1. generates narrow space charge regions at the contacts and an improved charge carriers' injection through an efficient tunnelling; 2. assures a low voltages across the transport layers because of the high conductivity. On the other hand, the "p" doping of the "n" conduction layer has a stabilization effect by trapping the positive charge carriers partially responsible for the degradation of the device (Zhi-Lin, 1998; Cheng, G, 2006).

3. Theoretical approach

Many theories have been proposed in the last years to describe charge injection into materials characterised by a hopping transport, such as organic compounds. The electrical transport theories in organics try to describe the charge injection process as thermally-assisted tunnelling from the metal to localized states (Abkowitz, 1995), tunnelling into polaron levels in polymers (Conwell, 1997), thermally-assisted injection into an energetically disordered dielectric (Arkhipov, 1998), or as diffusion-limited thermionic emission (Emtage, 1966; Scott, 1999). The most important factors playing a role in the injection of the charge carriers from metal to organic are the charge mobility in the organic layer (Emtage, 1966; Scott, 1999), the dependence of the mobility of the electric field intensity (Borsenberger, 1998) and of charge density (Roichman, 2002), the trapping of injected charge at the interface due to the image potential (Gartstein, 1996), the interface dipoles arising from the charge transfer (Crispin, 2002) or the interfacial chemistry (Abkowitz, 1998) and disorder in these interface dipoles (Baldo, 2001).
The simplest case to analyse can be a metal electrode that injects electrons in a trap free organic semiconductor. At lower voltages and neglecting the diffusion, the current is determined by the motion of the free electrons that are present in the semiconductor and the current density is given by the Ohm's law (Lambert, 1970):

$$J_{\Omega} = q\mu_0 N_0 \frac{V}{d} \tag{3.1}$$

where q is charge of the electron, N_0 is the number of free electrons per unit volume, μ is the mobility of electron, V is the applied voltage and d is the length of the sample (film thickness). In the case of purely injection-limited currents, neglecting the specific limiting mechanisms, the current at constant intensity field, E, has no explicit thickness dependence and is given by:

$$J=J(E) \tag{3.2}$$

The transport over an interfacial barrier at a metal/semiconductor interface can be analysed with one of the following theories:

1. For the process thermally activated at room temperature, is used the thermionic, Richardson-Schottky (RS) emission (Sze, 1981; Ashcroft, 1976) over the barriers to describe the transport characteristics.
2. For tight barriers at low temperatures, electron tunnelling or Fowler-Nordheim (FN) tunnelling (Sze, 1981) dominates the transport process.

The (RS) model is based on the lowering of the energetic barrier height by the image charge potential under the effect of an external electric field of intensity $E=V/d$. In this model, the current density J_{RS}, as a function of field intensity, is given by the equation:

$$J_{RS} = A^{*}T^{2}\exp\left(-\frac{\phi_B - \beta_{RS}\sqrt{E}}{k_B T}\right) \tag{3.3}$$

where: $A^{*} = 4\pi q m^{*} k_B^2 / h^3$ [A*=120 A/cm²K² for m*=m_0 (electron mass)] is the Richardson constant (q=electron charge, k_B=Boltzmann constant; h=Planck constant, T= Thermodynamic temperature); $\beta_{RS} = \sqrt{q^3/4\pi\varepsilon\varepsilon_0}$ (ε is the relative permittivity and ε_0 is the vacuum permittivity) and Φ_B is the zero-field injection barrier.

In the case of FN tunnelling model, the Columbic effects are neglected. It is considered the tunnelling through a triangular barrier into a continuum of states. In this model the current density is given by the following equation (Gao, 2002):

$$J_{FN} = \frac{A^{*}q^2E^2}{\Phi_B \alpha^2 k_B^2}\exp\left(-\frac{2\alpha\Phi_B^{3/2}}{3qE}\right) \tag{3.4}$$

Under certain conditions, the (RS) and (FN) models can be applied to explain the conduction also in inorganic semiconductors characterized by extended band states and large mean free path.

At low voltages, and neglecting the diffusion, the current is determined by the motion of the free electrons and the current density is given by the Ohm's law. As the voltage increases, electrons injected from the contact begin to exceed the electrons that are initially present inside the semiconductor. This happens when the charge corresponding to the number of electrons becomes approximately equal to $C \cdot V$, where C is the capacitance of the sample and V is the applied voltage. This is the space charge limited (SCL) regime and the Mott-Gurney (Mott, 1940; Shen, 2004) equation can be applied for SCLC for field-independent mobility and the current density expression becomes:

$$J_{SCLC} = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3} \tag{3.6}$$

where $\varepsilon\varepsilon_0$ is the permittivity of the organic. The threshold voltage, V_0, at which the current turns from ohmic to SCL can be found by the relation:

$$V_0 = \frac{8}{9}eN_0\frac{d^2}{\varepsilon\varepsilon_0} \tag{3.7}$$

The SCL conduction relies on a phenomenological theory developed in the 1950s and subsequently improved with more specific details (Lampert, 1970; Kao, 2004).
Considering a trap free semiconductor with a limitation of the current imposed only by the space charge (SCLC), with the mobility depending or being independent of the field intensity, the current at constant intensity field becomes

$$J = J^*(E)/d \tag{3.8}$$

where d is the thickness of the layer as mentioned above.
Space charge limited transport appears in undoped, wide-gap semiconductors in which the density of charge carriers at equilibrium is very small (de Boer, 2005). In these materials the current is generated by the charge injected from the contacts. The density of the charge carriers is determined (limited) by the electrostatic phenomena.
Especially in amorphous molecular materials, molecularly doped polymers and most of the conjugated polymers, the mobility is characterized by a field-dependence and an approximate analytical expression has been deduced (Murgatroyd, 1970). This is the Poole-Frenkel (PF) field dependence of the mobility:

$$\mu(E) = \mu_0 \exp\left(\beta\sqrt{E}\right) \tag{3.9}$$

where μ_0 is the zero-field mobility, E is the electric field strength and β is associated with the Poole-Frenkel-like field dependence of the mobility in the organic (Silveira, 2004). For field dependent mobility the SCL current density becomes:

$$J_{SCLC} = \frac{9}{8}\varepsilon\varepsilon_0\mu_0\frac{V^2}{d^3}\exp\left(0.89\beta\sqrt{V/d}\right) \tag{3.10}$$

Measuring the current as a function of voltage it was remarked a transition from „ohmic" conduction J_Ω at low voltage to a SCL conduction at high voltages, with the corresponding, low voltage, current densities J_Ω given by:

$$J_\Omega = \mu_0 N_0 \frac{V}{d}\exp(\beta\sqrt{V/d}) \tag{3.11}$$

where N_0 is the density of free carriers and J_{SCL} is given by Eq. (3.10).
The conduction in organic semiconductors can be injection-limited or transport-limited (Boer, 2005). For injection-limited conduction the models for bulk-limited transport, such as trap charge limited transport (Burrows, 1996; Lampert, 1970; Campbell, 1998; Campbell, 1997; Hung, 1997; Parker, 1994; Sze, 1981) and space charge limited transport with a field and temperature dependence of the mobility (Bloom, 1997) can not be applied.
For a bulk-limited transport such as the trap charge limited conduction (TCLC), with an exponential trap distribution and a mobility independent of field, the current at constant field varies with d^{-l} with l>1 (Lampert, 1970; Kao, 1981):

$$J = J^*(E)/d^l \tag{3.12}$$

The bulk-limited transport explains both the thickness and temperature dependences of current-voltage characteristics over many order of magnitude and the variations in injection

for different cathode materials. This model can not explain the dependence of current-voltage characteristics on the composition of the injection contact (Baldo, 2001).
The shape of the I-V curves can be the result of the conjugated effect of the surface and bulk traps and not of different physical mechanism (de Boer, 2005).
In the case of Poole-Frenkel field dependence of the mobility, SCLC can show exactly like TCLC, for the current versus voltage curve, a power law behaviour, but the power coefficient is higher than 2. The distinction between these two mechanisms can be done by the difference in the thickness dependence of these mechanisms given by Eq. (3.8) and Eq. (3.12) respectively.

4. Experimental

4.1 Types of substrates

To investigate the electrical conduction properties of the interface inorganic/organic and organic/organic have been prepared sandwich type heterostructures on different substrates: ITO with different sheet resistance and single crystal silicon with different types of conductibility, p and n, and different resistivity, and a given degree of surface processing [double side etched (E/E)]. Single silicon wafers (Si) could be used as an ohmic charge carrier injection contact for organic compounds of high ionization energy (high value of HOMO) because of the promising properties such as the high mobility of the charge carriers, the possibility to be p and n doped and because of reduced surface reactivity and interfacial interactions obtained by chemical processing by etching.
Theoretically, the hole/electron injecting contacts must be metals with high/low work function to reduce the height of the injection barriers (Hill, 1998). An efficient injection of holes into a p-type conduction organic semiconductor is possible from an ITO semiconductor layer characterized by a work function situated between 4.6 eV and 5 eV. If the effective electrode work function is higher than the ionisation energy of the organic semiconductor, the contact has an ohmic behaviour and the charge carriers are injected from electrode to organic. The main difficulty is associated with the high value for the ionisation energy (HOMO), higher than 5.5 eV, in some p type conduction organic semiconductors.

4.2 Organic thin films preparation

Beside the wide band gap organic semiconductors [benzil, meta-dinitrobenzene (m-DNB)] studied for the first time from the point of view of the films' electrical properties, other organic semiconductors, which have attracted a great research interest, were:
perylene: IE=5.1 eV (Kang, 2005), Eg=2.5 eV (Kang, 2005); **3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA):** IE=6.2 eV (Gao, 2003), IE=6.8 eV (Gao, 2001), Eg=2.2 eV (Rajagopal, 1998); **tris (8-hydroxyquinoline) aluminium (Alq3):** IE=5.7 eV (Hirose, 1996), IE=5.95 (Gao, 2001), EA=3.25 eV (Rajagopal, 1998); **zinc phthalocyanine (ZnPc):** IE=5.28 eV (Gao, 2002), Eg=1.94 eV (Gao, 2001; Gao, 2003); **N,N'-di-[(1-naphtalenyl)-N,N'-diaphenyl]-(1,1'-biphenyl)-4,4'diamine (α-NPD):** IE=5.52 eV (Gao, 2003), Eg=3.1 eV (Rajagopal, 1998); **5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine synthetic (TPyP):** EA=4.1 eV (Antohe, 2008), Eg=2.7 eV, evaluated from the UV-VIS transmission spectra of the thin films (Rasoga, 2009).
Two different methods have been used to prepare organic molecular thin films: 1. the rapid directional solidification method and 2. the vacuum evaporation and deposition method.
It is adequate to grow films from organic compounds with a melting point $T_{melting}$<100°C between two silicon wafers using a temperature gradient for solidification ΔT>50°C to

counteract the supercooling that characterises the large molecule organic compounds (Stanculescu, 2004; Stanculescu, 2006b; Stanculescu, 2006c). This method has been also used for the preparation of doped organic semiconductor layer. As dopants have been used oxine (8-hydroxyquinoline) or resorcinol (1, 3 dihydroxybenzene) in m-DNB and Na or Ag or m-DNB in benzil (Stanculescu, 2005; Stanculescu, 2006 b).
Thin films of organic molecular compounds with $T_{melting}$>100 °C have been prepared by vacuum evaporation and deposition processes that allows the preparation of stable, homogeneous films with a specified geometry and a good adhesion to the substrate (Stanculescu, 2006 a; Stanculescu, 2008; Rasoga, 2009).

4.3 Organic multilayer heterostructures manufacturing

Organic multilayer heterostructures have been realised using two different procedures. The successive organic layers have been prepared by vacuum evaporation and deposition using aluminium foil masks. The metallic contact has been obtained by sputtering or vacuum evaporation of the metal.

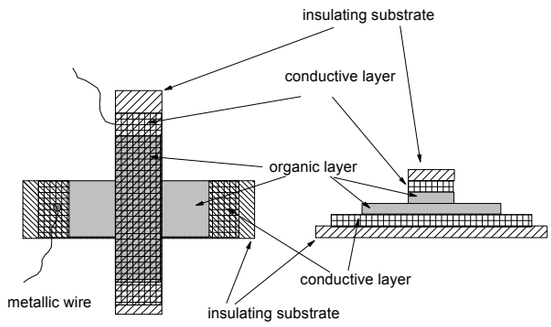


Fig. 4.1. Schematic cross section through the following heterostructures: insulating substrate (glass, organic insulator), conductive layer (Al, Cu, Si, ITO), organic single or double layers, insulating substrate (Stanculescu, 2007 b)

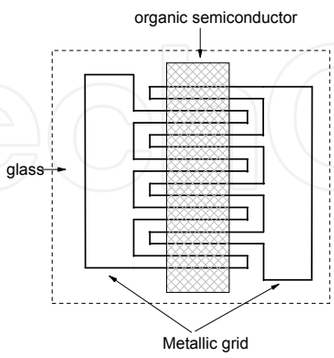


Fig. 4.2. Planar grid contact geometry (Stanculescu, 2007 b)

Semiconductor/Insulator/Semiconductor (SIS) sandwich type Si/single or double organic layer/Si structures and Metal/Insulator/Semiconductor (MIS) sandwich type (Cu or Al)/ single or double organic layer/Si or ITO structures have been prepared by a process in two steps.

Firstly have been manufactured the inorganic/organic (SI) junctions and metal/organic (MI) junctions and subsequently the SIS and MIS heterostructures putting into direct contact the organic film of two (SI) or, one (SI) and one (MI) individual junction as it is shown in Figure 4.1 (Stanculescu, 2007 b; Stanculescu, 2008).
Metal Insulator Metal (MIM) heterostructures have been prepared by the deposition of Al electrodes with a special grid configuration, presented in Figure 4.2, on glass substrate followed by the deposition by vacuum evaporation of the organic thin film.

5. Electrical conduction in organic molecular compounds heterostructures

5.1 SIS type structures: inorganic /organic /inorganic (Si/organic/Si)

When the order is induced by the substrate, the molecular planes of PTCDA have a preferred orientation and the (102) planes form stacks with small interplanar spacing, perpendicular to the substrate (Wu, 1997). This arrangement in the solid state generates a significant overlap of the π orbitals of the aromatic rings belonging to molecules situated in different planes. In Alq3 the conduction properties depend on the dominant type of stereoisomer, meridian or facial (Cölle, 2003), and are generated by the overlapping degree of the π orbitals of the hydroxyquinoline ligands belonging to the neighbouring molecules.

5.1.1 Si/wide band gap organic semiconductor/Si heterostructures

The wide band gap organic semiconductors used for the thin film deposition have different particularities of the molecular configuration: 1. one aromatic ring and two NO_2 substituent groups, meta-dinitrobenzene (m-DNB); 2. two aromatic rings coupled by two CO substituent groups, benzil (known also as diphenyl-α,β-diketone, diphenylethanedione, dibenzoyl). In Figure 5.1 and Figure 5.2 can be seen that the value of the current is comparable for the both types of structures prepared with non-purified compounds: ~ 10^{-6} A for an applied voltage of 1 V.
For the structures based on organic layers prepared by rapid solidification in the experimental conditions mentioned above in paragraph 4, it has been remarked a non-ohmic behaviour at low voltages. Some differences have been evidenced in the shape of the I-V curves for the structures prepared with m-DNB and benzil and presented in Figure 5.1 and Figure 5.2. The origin of these differences could be in the different molecular structures of the two compounds, which are reflected in different crystalline quality of the layers.
Despite the fact that a linear behaviour has been expected at low voltages for an organic molecular film grown between two Si electrodes a deviation from the ohmic dependence has been obtained, which can be explained by two counteracting mechanisms. The high value of the ionization energy in some of the benzene derivatives [higher than 5.5 eV (Hersberg, 1959)] means deep HOMO levels. This position of the energetic level favours the accumulation of the charge carriers near the surface and as consequence an ohmic dependence. But this effect is dominated by the very low mobility of the charge carriers in these organic molecular compounds that favours the generation of the space charge and a limitation of the current by this mechanism, leading to non-linear I-V dependences.
In m-DNB and benzil the conduction is favoured by the strong interaction between the electrons of different substituent groups (NO_2 or CO). In the solid state these groups are close one to another and assure a higher mobility of the charge carriers and a weaker influence on the current of the space charge limitation.

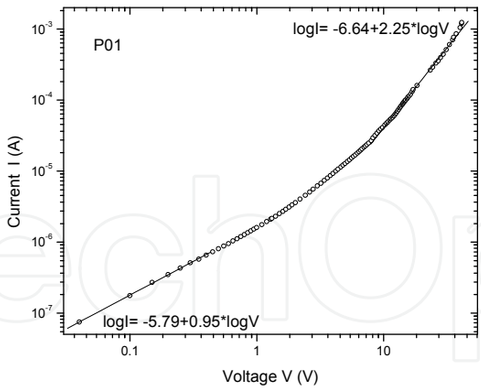


Fig. 5.1. I-V plot for as-synthesised m-DNB layer grown between two Si wafers, Si(p), E/E, ρ=12-15 Ωcm, (P01 in Table 1) (Stanculescu, 2006 b)

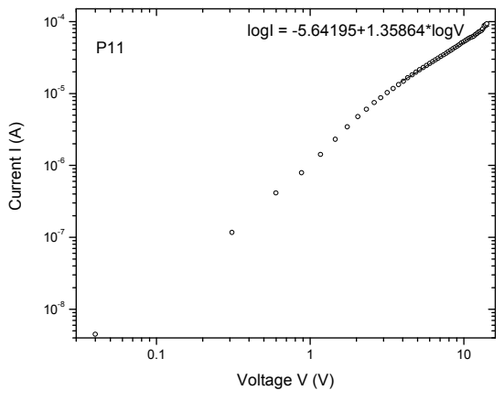


Fig. 5.2. I-V plot for as-synthesised benzil layer grown between two Si wafers, Si(p), E/E, ρ=5.5-27 Ωcm, (P11 in Table 1) (Stanculescu, 2006 b)

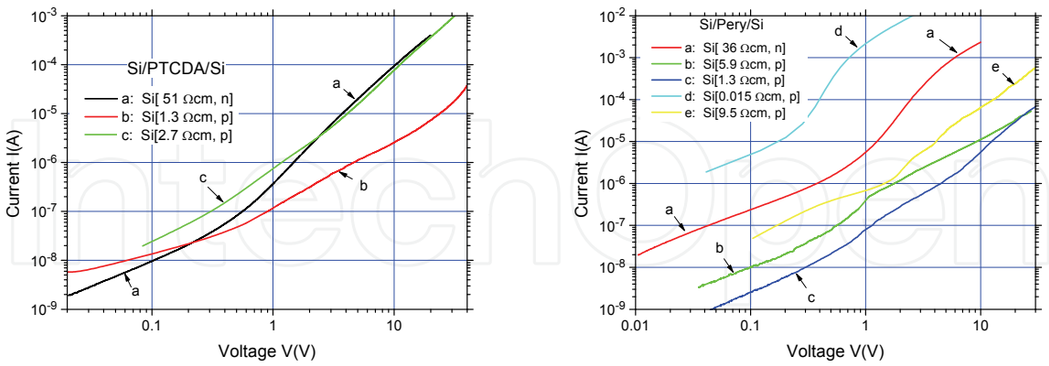
The interactions between the molecules are stronger in m-DNB than in benzil because the group NO_2 in m-DNB has a stronger polar character compared to the group CO in benzil and favours the overlapping between the π orbitals of the neighbour molecules. As a consequence, m-DNB is a compound characterized by a narrow electronic band structure with a high delocalization for electrons and holes that assures an increase in the electrical conduction (Stanculescu, 2006 b). The moderate polar character of the CO groups in benzil is correlated with a lower overlapping of the π orbitals and a higher degree of localization of the charge carriers. This generates a slightly wider electronic band structure of the compound (benzil) and a slightly lower conductivity.

5.1.2 Si/ molecular organic/Si

The type of molecules stacking in the organic solid state is very important for the electrical behaviour of the organic semiconductor because it could favour the significant overlapping between the π electrons clouds supporting the charge carriers generation and transport. This

leads to a significant delocalisation of the charge carriers and, as consequence, to a relatively significant intrinsic conductivity.
Perylene and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) are characterised by a special stacked arrangement with distances between the parallel planes of molecules of 3.46 Å (Hirose, 1996) and 3.21 Å (Wu, 1997) respectively. This stacking assures significant overlapping between the π electrons clouds of the neighbouring molecules from successive planes and sustains a stronger intermolecular coupling in the direction perpendicularly to the substrate. This way are favoured highly anisotropic electrical transport properties. The charge carriers transport in the direction parallel to the molecular plane of perylene and PTCDA is limited by the distance between the adjacent molecules and by the polar binding of the hydrogen and oxygen atoms.
To investigate the injection properties of these organics at the contact with different types of single crystal Si electrodes, the position of the energy level in Si and in organic must be compared: the energy of the holes in the valence band of the p type silicon (E_{VB}~5.1 eV) must be compared with the energy of the HOMO level of the organic compound, and the energy of the electrons in the conduction band of the n type silicon (E_{CB}~4 eV) must be compared with the energy of the LUMO level of the organic compound.
It can be anticipated from theoretical considerations that a higher number of holes is injected from the p type silicon in Si/perylene/Si heterostructure because of the small difference between the energy of the valence band level in Si situated around 5 eV and the energy of the HOMO level in perylene, an organic compound characterized by an ionisation energy of IE=5.1 eV (Hirose, 1996).
Experimentally data obtained for low applied voltages (~ 0.1 V) presented in Figure 5.3 a and Figure 5.3 b show a slightly higher value of the current passing through the Si/PTCDA junction (10^{-8} A) compared to Si/perylene junction (4×10^{-9} A), when the both structures are prepared with the same type of Si electrode (p type conduction, resistivity of 1.3 Ωcm). This confirms that a lower number of charge carriers are injected in perylene because of the surface states. The specific interaction of the organic molecules with the Si surface, such as surface adsorption, is important in the generation of the injection barrier and can significantly change the electronic properties of the Si surface.
For the structure realised with n type Si electrodes we have anticipated an increase in the number of electrons injected in PTCDA determined by the lower position of the energetic level associated with the electron affinity in PTCDA, calculated using IE given in paragraph 4.2, EA=4 eV or EA=4.6 eV compared to perylene, EA=2.6 eV. The band gap energy was considered Eg=2.2 eV in PTCDA (Rajagopal, 1998) and Eg=2.5 eV in perylene (Kang, 2005).
For n type of Si electrodes and an applied voltage of 1 V, the current obtained experimentally in Si/perylene/Si structures, drawn in Figure 5.3 b, is one order of magnitude higher than the current obtained in Si/PTCDA/Si structures drawn in Figure 5.3 a.
A steeper increase in the current at voltages higher than 0.1 V, presented in Figure 5.3 b, has been obtained using as electrodes p type, low resistivity silicon wafers, ρ=0.015 Ωcm. This behaviour can be explained by the high density of defects, which characterizes the low resistivity (highly doped) silicon, that could be induced in the organic layer.
For the heterostructure with two n type Si electrodes, the difference between the current, at forward and reverse bias, at a given voltage, is very small and the contact Si/perylene is practically ohmic at voltages lower than 1 V, as shown in Figure 5.4. At low voltages (0.1-1 V), the slope of the logarithmic I-V characteristics is n=1, meaning that the behaviour of the above mentioned structures is ohmic and the current is not limited. In this case, the

accumulation of the charge carriers is not so significant and the injection of the charge carriers is not reduced by the created electrostatic field.



(a) organic-PTCDA; (b) organic-perylene

Fig. 5.3. I-V characteristics for Si/organic/Si heterostructures for different Si electrodes (Stanculescu, 2008)

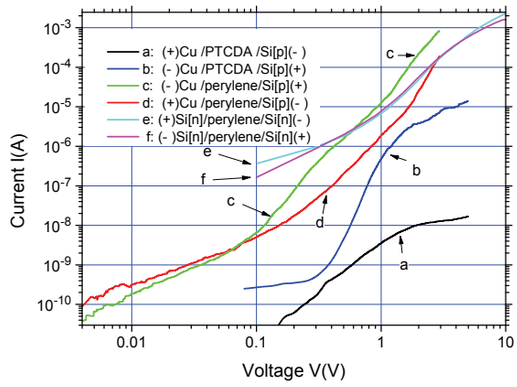


Fig. 5.4. I-V characteristics of Cu(Si)/perylene(PTCDA)/Si heterostructures at forward and reverse bias (Stanculescu, 2008).

Because a Poole-Frenkel (PF) mechanism characterised by n=1/2, which involves the field dependence of the mobility, has not been evidenced, the conduction could be space charge limited (without electric field dependence of the mobility) and trap charge limited (Gao, 2002). In the higher applied voltages region (> 1 V) the charge transport process appears to be space charge limited, SCLC (n=2) when the charge injected from the inorganic electrodes (Si) is larger than the charge existing in material in equilibrium, and trap charge limited, TCLC (n>2) when exist discrete trapping levels associated with defects in the organic layer. A transition region situated around 1V has been evidenced in the region where the conduction process is trap charge limited, being associated with a mechanism of trap filling.
The general shape of the I-V characteristics is not very different for structures realized with n type Si and n type conduction organic molecular compounds, n type Si/TPyP or n type Si/Alq3, as can be seen in Figure 5.5. The current is less than one order of magnitude higher in TPyP based heterostructure compared to Alq3 based heterostructure for an applied voltage lower than 1 V.

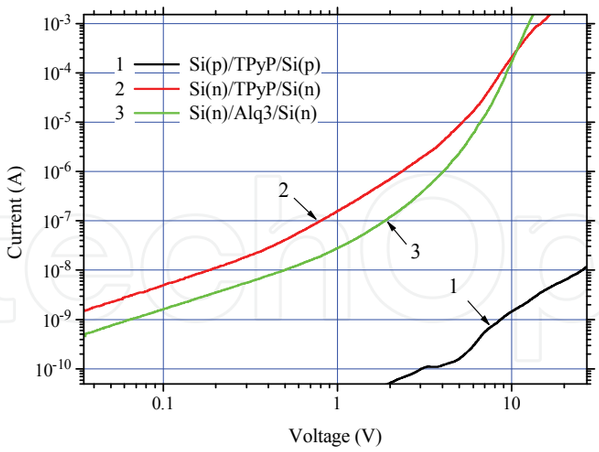


Fig. 5.5. I-V characteristics for SIS symmetrical heterostructures based on single n type organic thin film (Rasoga, 2009):
1. Si(Cz, E/E, p: 1.34 Ωcm)/TPyP/ Si(Cz, E/E, p: 1.34 Ωcm);
2. Si(Cz, E/E, n: 0.008 Ωcm)/TPyP/ Si(Cz, E/E, n: 0.008 Ωcm);
3. Si(Cz, E/E, n: 0.008 Ωcm)/Alq3/ Si(Cz, E/E, n: 0.008 Ωcm)

A higher number of injected electrons was obtained in TPyP with E_{LUMO}~4.1 eV (Antohe, 2008) compared to Alq3 with E_{LUMO}=3.25 eV (Rajagopal, 1998). This behaviour is sustained by the position of the electron affinity (LUMO) level in TPyP compared to the position of the conduction band level in silicon. The difference between the energy of the conduction band in n type Si and the energy of the electron affinity is higher in Alq3 (ΔE~0.75 eV) compared to TPyP (ΔE~0.10 eV). The height of the energetic barrier favours the injection of the electron at the contact n type Si/TPyP. As it is shown in Figure 5.5, for an applied voltage of 1 V, the interface between n type Si wafer and n type conduction organic semiconductor (TPyP, Alq3) favours the injection of a much higher number of charge carriers, $I_{TPyP}=1.5\times10^{-7}$ A and $I_{Alq3}=2.5\times10^{-8}$ A, than the interface between p type Si wafer and the same n type conduction organics (I_{TPyP} is lower than 10^{-10} A).
The lower injection at the contact n type Si/Alq3 compared to the contact n type Si/TPyP could be explained by the lower efficiency of the coupling between the n type Si substrate and the π electrons system of Alq3 compared to TpyP (Rasoga, 2009).
The number of charges injected at the contact p type Si and p conduction organic, Si/ZnPc, is higher (6×10^{-4} A at an applied voltage of 1 V) because ZnPc (as PTCDA as well) is a planar aromatic molecule characterised by a preferred orientation of the molecular planes and small distances between the intermolecular planes (Wu, 1997).

5.1.3 Si/organic multilayer/Si heterostructures

The order of preparation of organic/organic structure in multilayer heterostructures is not critical because the system is not submitted to high thermal variations during the vacuum evaporation process. The behaviour of the interface organic/organic has an important influence on the shape of the I-V characteristics by a charge accumulation process. Figure 5.6 shows the I-V characteristics for the structures with double organic layer, n type organic semiconductor (TPyP or Alq3) on p type organic semiconductor (PTCDA or perylene). The

highest value of the current, was obtained for an applied voltage of 1 V at reverse polarization (n type Si electrode positively biased and p type Si electrode negatively biased) in the heterostructures Si/TPyP/PTCDA/Si (I=8×10^{-6} A) and Si/Alq3/perylene/Si (I=5×10^{-6} A).
The energetic barriers for the charge carriers at the p-n junction results from the value of the ionisation energy and electron affinity for each organic compound:

$\Delta E_{TPyP/PTCDA}$~0 eV; $\Delta E_{Alq3/PTCDA}$=0.85 eV; $\Delta E_{TPyP/perylene}$=1.7 eV; $\Delta E_{Alq3/perylene}$=0.85 eV. (holes)

$\Delta E_{TPyP/PTCDA}$~0 eV; $\Delta E_{Alq3/PTCDA}$=1.35 eV; $\Delta E_{TPyP/perylene}$=1.5 eV; $\Delta E_{Alq3/perylene}$=0.65 eV (electrons)

The position of the HOMO (IE) level in TPyP can be estimated from the position of the LUMO level (EA=4.1 eV) and the optical band gap (Eg=2.7 eV). The optical band gap has been evaluated from the optical transmission spectra of TPyP thin films deposited on quartz substrate.

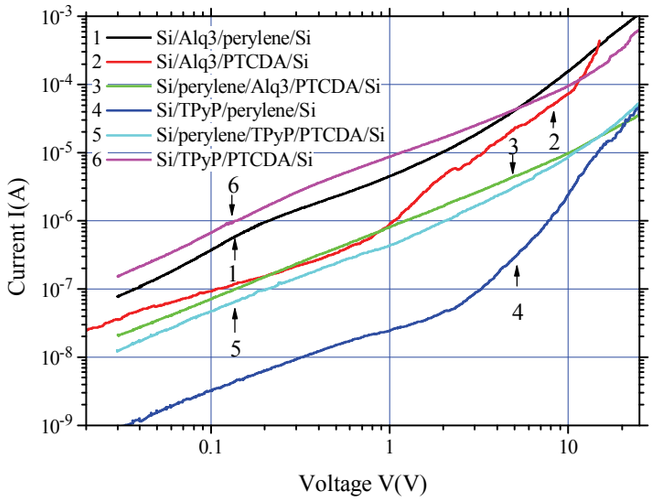


Fig. 5.6. I-V characteristics for SIS heterostructures based on double n-p organic thin films (Rasoga, 2009):
1. Si(Cz, E/E, n: 0.008 Ωcm)/Alq3/ perylene/Si(Cz, E/E, p: 6.78 Ωcm);
2. Si(Cz, E/E, n: 0.008 Ωcm)/Alq3/ PTCDA/Si(Cz, E/E, p: 1.34 Ωcm);
3. Si(Cz, E/E, p: 1.34 Ωcm)/perylene/ Alq3/PTCDA/Si(Cz, E/E, p: 6.78 Ωcm);
4. Si(Cz, E/E, n: 0.008 Ωcm)/TPyP/ perylene/Si(Cz, E/E, p: 1.34 Ωcm);
5. Si(Cz, E/E, p: 1.34 Ωcm)/perylene/ TPyP/PTCDA/Si(Cz, E/E, p: 1.34 Ωcm);
6. Si(Cz, E/E, n: 0.008 Ωcm)/TPyP/ PTCDA/Si(Cz, E/E, p: 1.34 Ωcm)

In the structures with three organic layer perylene/Alq3/PTCDA, presented in Figure 5.6, the currents are slightly different at the reverse bias (p type, ρ=1.34 Ωcm Si electrode positively biased and p type ρ=6.78 Ωcm Si electrode negatively biased) compared to the structure with only two organic layers, Alq3/PTCDA at reverse bias (p type, ρ=1.3 Ωcm Si electrode, negatively biased and n type, ρ=0.008 Ωcm, positively biased).
The supplementary perylene layer decreases with more than one order of magnitude the value of the current at an applied voltage of 1 V in the heterostructure Si/TPyP/PTCDA/Si.

This is a result of the high energetic barrier at the contact perylene/TPyP (ΔE=1.7 eV). In the structure Si/Alq3/PTCDA/Si, a supplementary perylene layer has no influence on the current for applied voltages lower than 1 V. The effect of the energetic barrier height at the contact perylene/Alq3 (ΔE=0.85 eV) becomes important in the heterostructure Si/perylene/Alq3/PTCDA/Si at applied voltages higher than 1 V (Rasoga, 2009).

5.2 Effect of the dopant

The doping process, which refers to the introduction of a strong electron donor or acceptor in the host organic matrix, could have a strong impact on the material properties, increasing the electrical conductivity of these host compounds and involving or not charge transfer between the organic host matrix and the guest dopant (organic or inorganic). For example, by the intercalation of benzil matrix with monovalent alkali (sodium) or non-alkali (silver) metallic atoms can be induced delocalised charge carriers, electrons and holes, respectively. Similarly results are expected for organic dopants containing substituent groups on the aromatic nucleus with strong electron donors (such as OH) or acceptors (such as NO_2 and CO), properties.

The organic molecular films show some particularities of the transport mechanism of the charge carriers, small amount of impurity or dopant strongly affecting or even masking or hiding the intrinsic properties by a trapping mechanism.

It has been evidenced that the relatively low intrinsic conductivity of optical wide-gap organic semiconductor, benzil [Eg=2.84 eV (Stanculescu, 2004; Stanculescu, 2006 a] and m-DNB [Eg=2.92 eV (Stanculescu, 2004; Stanculescu, 2006 a)] has been improved by doping: in benzil doped with m-DNB and, in m-DNB doped with 8-hydroxyquinoline (oxine) or 1,3 dihydroxybenzene (resorcinol). In these situations the resistivity of the organic layer decreases to 10^6-10^7 Ωcm. New states have been generated within the band gap by doping, which can be involved in the conduction process.

Benzil can be easily doped with electrons donors such as alkali metals (sodium) because it is characterized by a high electron affinity. At low concentration, c=1 wt %, it was evidenced an increased conductivity compared to the pure compound.

Another factor with an important effect on the electrical properties of the heterostructures is the crystalline quality of the intermediate organic layer. An increase in the resistivity is obtained for higher concentration of sodium, c=6 wt %, or by p type doping with silver. A high concentration of dopants can induce a higher concentration of defects. Microstructured patterns of the organic crystalline layers are created either by dopants or by the grain boundaries whose generation is controlled by the thermal regime of the solidification process. The effect of dopant on the resistivity of the organic layer is presented in Table 1.

The heterostructures prepared with doped intermediate benzil layer show a non-linear behaviour of the I-V characteristics, as illustrated in Figure 5.7.

We have emphasised a special behaviour for the organic layer doped with organic molecule. In benzil doped with m-DNB (3 wt %) we have obtained an important decrease in resistivity and a higher conductibility. m-DNB doped with resorcinol shows a different I-V characteristic. The exponential dependence can be correlated with a field intensity dependence of the mobility of the charge carriers.

An even stronger effect of the dopant over the resistivity of the organic layer is evidenced in m-DNB. The resistivity of the m-DNB layer can be reduced with three orders using, as dopants, oxine (c=1 wt %) or resorcinol (10 wt %) as mentioned in Table 1.

An exponential dependence between I and $\sqrt{V}$ has been evidenced in Figure 5.8 for m-DNB layer highly doped with resorcinol (10 %), in the low voltage range, around 1 V, suggesting a Poole-Frank conduction mechanism involving the field dependence of the charge carrier mobility (Silveira, 2005) :

$$I \sim V \cdot e^{C\sqrt{V}} \tag{5.1}$$

Sample	Organic material	Film thickness (μm)	Si conductivity type	Si surface processing	Resistivity of the organic film ρ (Ωcm)
P01	m-DNB as synthesized	21	p	E/E	2.1×10^{9}
P03	m-DNB purified by melting zone	16	p	E/E	6.6×10^{9}
P07	m-DNB+oxine	75	n	E/E	0.49×10^{6}
P08	m-DNB+resorcinol	20	n	E/E	5.3×10^{6}
P11	benzil as synthesized	52	p	E/E	0.76×10^{9}
P12	benzil purified by melting zone	17	p	E/E	5.0×10^{9}
P15	benzil+m-DNB	30	p	E/E	2.3×10^{7}
P17	benzil+1 wt % Na	44	p	E/E	0.79×10^{9}
P18	benzil +6 wt % Na	43	p	E/E	1.9×10^{10}
P19	benzil+2.4 wt % Ag	72	p	E/E	4.5×10^{10}

Table 1. The properties of prepared SIS heterostructures (Stanculescu, 2006 b)

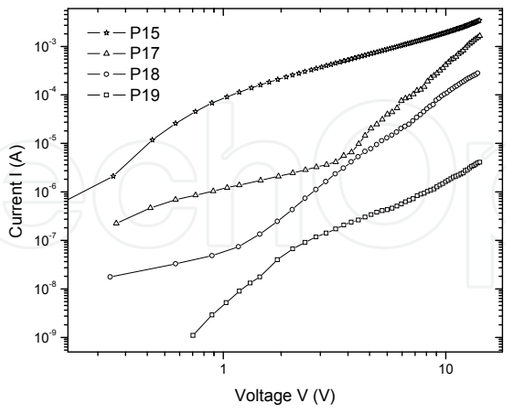


Fig. 5.7. I-V plots (Stanculescu, 2006 b) for:
a) benzil doped with 1 wt% Na, Si(p), (P17);
b) benzil doped with 6 wt% Na, Si(p), (P18);
c) benzil doped with 2.4 wt% Ag, Si(p), (P19);
d) benzil doped with 3 wt% m-DNB, Si(p), (P15)

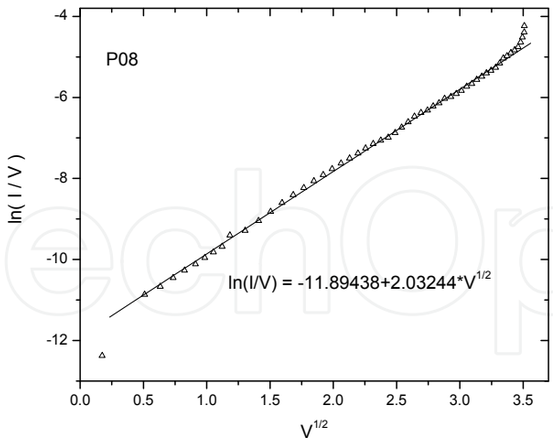


Fig. 5.8. The plot $\ln(I/V) - \sqrt{V}$ for a layer of m-DNB highly doped (10 wt%) with resorcinol grown between two Si wafers, Si (n), E/E, ρ=0.90-1.9 Ωcm, (P08 in Table 1) (Stanculescu, 2006 b)

6. Effect of metallic contact on the electrical properties of organic semiconductor thin films

The charge carrier injection at this type of interface is more complicated than at the interface metal/inorganic semiconductor because in this case, the contact properties can be influenced by the defects induced on the organic surface by the metallic contact and by the space charge effect that characterises the organic semiconductors, effect that can obscure or alter the real contact properties (Stanculescu, 2007 a).
The injection efficiency at the interface metal/organic semiconductor depends on many factors such as the energetic barriers, which must to be overcome by the charge carriers, the morphology and composition of the interface. Diffusion processes or reaction tacking place at the interface could also influence the behaviour of the metal/organic contact (Hirose, 1996). When the physical contact between metal and organic solid is realized, interface states are induced by metallization or interdiffusion (Hirose, 1996).

6.1 MIS type structures: metal/organic semiconductor/inorganic semiconductor

Different types of structures have been investigated from the point of view of the electrical conduction properties. In the structures based on perylene and PTCDA the organic layer has been obtained by vacuum deposition, while in the structure based on wide band gap organic semiconductor, with $T_{melting}$ < 100 °C, Cu/m-DNB/Si, by rapid directional solidification between two substrates one of Si and the other of an organic insulator substrate covered with Cu (Stanculescu, 2007 a).
The order of the steps for the deposition of the layers that compose the heterostructure (metal on organic or organic on metal) can be very important for the behaviour of the heterostructure (Hill, 1998). The chemisorption of the organic molecules in determined sites controlled by the extended π-electrons system irrespective of the functional groups appear when the organic layer is deposited on a metallic layer. When a metal is deposited on an organic layer an important modification of the interface may take place as a result of the

chemical reaction between the metal and the organic molecules and/or of diffusion of a large number of metallic atoms into the organic layer. These processes generate a high density of states in the organic semiconductor band gap (Hill, 1998).
The diffusion into the organic layer depends on the type of metal and plays an important role in the behaviour of the metal/organic contact. The main difference between different metals is generated by the degree of diffusion of the metal atoms in the organic film. The diffusion process depends on the reactivity of the metal atom with the organic compound. The reactivity of the organic molecule is strongly dependent on the molecular structure. The groups that substitute the hydrogen to the aromatic nucleus, and sometimes the ends groups like anhydride in the case of PTCDA, control the interaction of the metal with the organic molecule.
For perylene or perylene derivative (such as PTCDA) the transport of the charge carriers at the contact metal/organic is influenced by the properties of the single silicon electrode and by the polarization of the heterostructure. A low height injection barrier is sustained by a value of the metallic cathode work function (Φ) close to the value of the electron affinity of the organic. This assures a high level of electrons injection from metal to the organic layer.
Some studies have mentioned In with the work function, Φ_{In} =4.2 eV (Hirose, 1996) and Al with Φ_{Al}=4.25 eV (Hirose, 1996), as the most adequate metals for contacting PTCDA (EA=4 eV or 4.6 eV depending on the reference).
For example, the distance between the molecular planes parallel to the substrate in PTCDA films is large compared to the metal atomic and ionic radius and assures a natural path for the motion of the metallic atom/ion in the organic crystalline layer of PTCDA. The motion is also facilitated by the local deformation of the organic crystalline lattice characterised by weak van der Waals bonds (Hirose, 1996). The motion of the metal atoms can also be influenced by the presence of defects, such as grain boundaries, which have influence on the structural quality of the film.
The chemical reaction between In or Al on one hand and PTCDA on the other hand involves predominantly the anhydride group of the organic molecule generating the oxidation of the adatoms and the reduction of C atoms from the carbonyl group, as a consequence of the high affinity of these metals for oxygen. The heat of formation of the reactive metals oxides is with orders of magnitude higher (ΔH_{298}=-1676 KJ/mol for Al_2O_3 and ΔH_{298}=-926 KJ/mol for In_2O_3) than the heat necessary for Ag_2O formation (ΔH_{298}=-31 KJ/mol) and the heat necessary for the formation of ordinary metal oxides. This means that the generation of In, and Al oxides take place in the detriment of metal-metal bonding, because the more negative is the heat of formation the more stable is the compound. This is due to the fact that more energy is lost to the surroundings when the compound is formed and the compound has a lower energy being more stable (Stanculescu, 2007 b).
For PTCDA, the attachment of the electronegative anhydride group to the perylene core causes the increase of the ionisation energy of perylene, IE=5.1 eV (Hirose, 1996). PTCDA has higher ionisation energy, IE=6.2 eV (Hirose, 1996) or IE= 6.8 eV (Gao, 2001) and electron affinity EA=4 eV or EA=4.6 eV respectively and its contact with metals are characterised by the transfer of the negative charge carriers (electrons) from metal (In, Al, Ag) to organic molecule (Hill, 1998).
The charged metallic ions created at the interface are driven through the materials by the electric field and can react with the organic molecule, depending on its chemical structure and reactivity. Considering Cu and Al metallic electrodes, the low atomic radius of Cu (1.57

Å) and Al (1.82 Å) compared to the distance of separation between the molecular planes (for compounds characterised by a nearly planar molecular configuration such as PTCDA and ZnPc) assures a structural way for the motion of metal atoms (ions) in this type of compounds.

This high diffusivity of metal atoms/ions can be attributed to a relatively low value of the first ionisation energy that favours the transfer of an electron to the host organic matrix, this ionisation leading to a Coulomb type repulsion between positively charged In ions situated in interstitials sites (organic crystalline materials are characterised by large dimension of the interstitials zones), acting as driving forces for diffusion. The diffusion rate is also substantial for the other selected metals (Al) but slowly decreases in the succession In>Al because the first ionisation energy for these metals increases in the following succession: 5.786 eV (In) < 5.985 eV (Al) (Stanculescu, 2007 b).

The reactivity of Al with perylene is not significant (there are not substituent groups to the aromatic nucleus), Al atoms diffuses through the perylene film characterised by a separation of 3.46 Å between the parallel plans of molecules (Hirose, 1996). At an applied voltage of 0.1-0.2 V has been remarked a region of transition though a region characterised by a power dependence between I and V. This power dependence with an exponent n=2 characterises the presence of the space-charge limited currents (SCLC) and with n>2 characterises the presence of the trap-charge limited currents (TCLC).

As can be seen from Figure 6.1, the I-V characteristics of the Si/perylene/Al heterostructure are not linear at low applied voltages (< 1 V) , but tend to an ohmic behaviour through a weak superlinear dependence at forward (direct) polarization at very low voltages (<0.03 eV). At reverse polarization, the I-V dependence is weak sublinear at voltages <1 V (Stanculescu, 2007a). As can be seen in Figure 6.1 for direct bias there is a region between 0.1 and 1 V characterised by power dependence with an exponent n>2. The region with power dependence (n>2) between I and V is present also for reverse bias but it is shifted between 1 and 10 V.

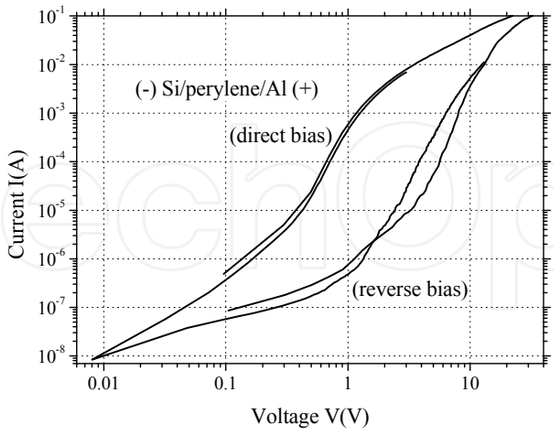


Fig. 6.1. I-V plot of Si/perylene/Al heterostructure (Stanculescu, 2007 a)

These experimental results confirm that the charge carriers transport by hopping and tunnelling mechanisms in the metal/organic semiconductor structure are favoured by the energetic states generated in the band gap by the diffusion of the metallic (Al; In) atoms and/or by the reaction taking place at the PTCDA (perylene)/Al(In) interface (Hirose, 1996).

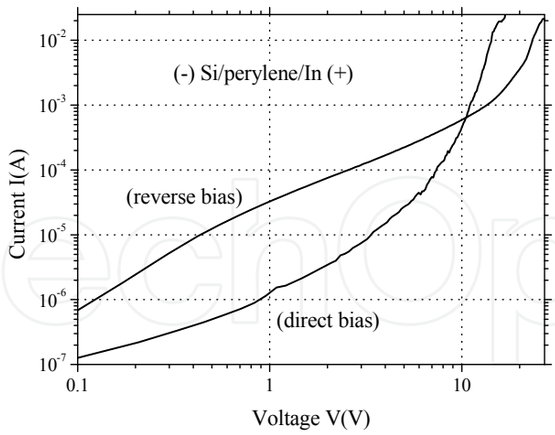


Fig. 6.2. I-V plot of Si/perylene/In heterostructure (Stanculescu, 2007 a)

The behaviour of the perylene/In contact is shown in Figure 6.2. In this case the reactivity of In is very weak, but the diffusion of In through the perylene layer is significant and induces states under the Fermi level. The ohmic character of this contact, associated with the charge carrier injection mechanism, evidenced at voltage lower than 2 V at direct bias and between 1 V and 10 V at reverse bias, can be explained by the conduction involving these states situated in the band gap, in the interface region, just below the Fermi level.

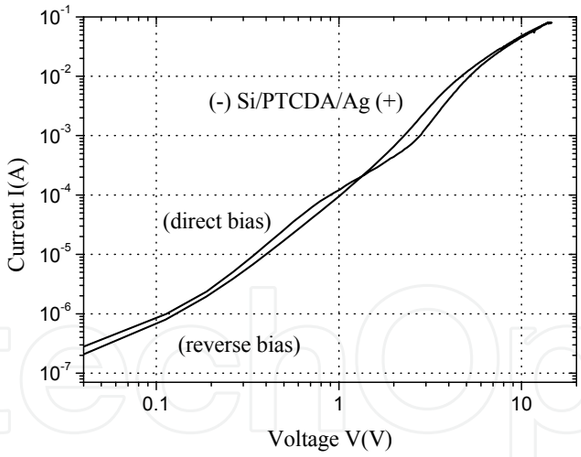


Fig. 6.3. I-V plot of Si/PTCDA/Ag heterostructure (Stanculescu, 2007 a)

The I-V characteristics of the PTCDA/Ag contact presented in Figure 6.3, are ohmic only at low voltages (<0.1 V), both at direct or reverse polarization. This can be explained by the reduced reactivity of silver with PTCDA molecule. The silver atoms are not inducing enough interface states in the band gap to be involved in the conduction process. The space charge limitation of the current (n=2) become important at slightly higher voltages (~ 0.1-1 V) both for forward and reverse polarization.

The quasi-linear I-V dependence of perylene/Ag contact shown in Figure 6.4, at applied voltages lower than 0.7 V, becomes a power dependence with n>2 suggesting the presence

of defects (traps) in the organic semiconductor band gap and the appearance of the TCLC phenomenon at applied higher voltages. In the region of quasi linear dependence between I and V the current has high value, between 10^{-6} and 10^{-5} A, that favours, in time, the degradation of the organic layer of the structure.

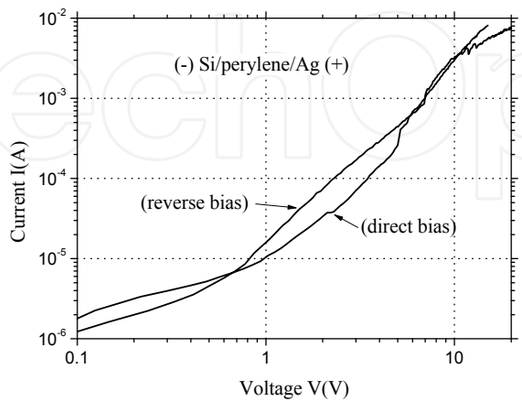


Fig. 6.4. I-V plot of Si/perylene/Ag heterostructure (Stanculescu, 2007 a)

The most important characteristic of In, Al and Ag diffusion process in organic layer is the high level of incorporation of isolated atoms and the absence of clustering process (Hirose, 1996).

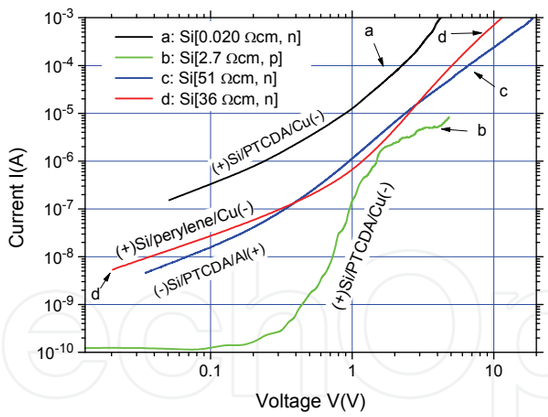


Fig. 6.5. I-V characteristics of metal/organic/Si heterostructures for different metallic electrodes and polarizations: metal-Cu, Al; organic-perylene, PTCDA (Stanculescu, 2008)

For silver and copper the situation is different because the relatively high first ionisation energy, 7.57 eV for Ag and 7.72 eV for Cu are not favourable to the diffusion in PTCDA as individual atoms, but are favourable to the clustering process. Another process that is favoured by these energetic considerations is the immobilization of the Cu atoms at the surface of the organic. The atoms of metals with high values of the first ionisation energy, such as Ag and Cu, remain neutral at the surface of the organic film and form cluster. The steeper increase in the current, that suggest the presence due to the effect due to the

interface beside the effect of the energetic barrier, has been evidenced in Figure 6.5 for the contact Cu/PTCDA [Φ_{Cu}=4.5 eV (Li, 2005)] at forward bias, (-) applied on Cu electrode and (+) on p type Si electrode.

For the heterostructure Cu/PTCDA/Si presented in Figure 6.5, with a semiconductor electrode of p type Si for an applied voltage of 0.4 eV, the current varied between 2×10^{-9} A at forward bias and 5×10^{-10} A at reverse bias, and for an applied voltage of 0.7 V, the current varied between 10^{-7} A at direct bias and 2×10^{-9} A at reverse bias showing a steep increase in current around 1 V.

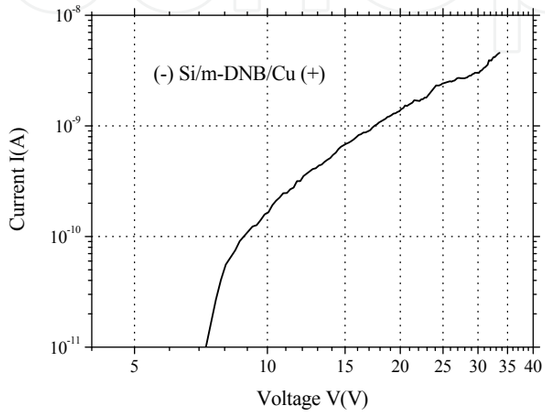


Fig. 6.6. I-V plot of Si/m-DNB/Cu heterostructure (Stanculescu, 2007 a)

For the heterostructure Cu/perylene/Si, for an applied voltage of 0.1 V no significant difference has been remarked between the current at direct and reverse bias (4-5×10^{-9} A). For an applied voltage of 0.4 V, the current varied between 2×10^{-6} A at forward bias and 2×10^{-7} A at reverse bias, suggesting a limiting behaviour of the metallic contact for applied voltages higher than 0.1 V. For n type Si electrode at voltages higher than 0.1 V, the current is higher, $I=3\times10^{-7}$ A in the heterostructure containing the contact Cu/PTCDA at forward bias, than in the heterostructure containing the contact Al/PTCDA [Φ_{Al}=4.28 eV (Eastment, 1973)], $I=2\times10^{-8}$ A, at reverse bias, as it is presented in Figure 6.5.

A distinct type of heterostructure Si/m-DNB/Cu presented in Figure 6.6 is characterised by a strong increase in the value of the current for voltages between 7 V and 10 V. For higher voltages situated between 10 and 20 V the behaviour of the I-V characteristic is close to linear.

Modifications in the I-V characteristics can be determined by modifications in the morphology of the film which are correlated with the preparation conditions. The preparation conditions are critical especially for the heterostructure based on rapid directional solidified films of m-DNB.

6.2 MIM type structures: metal/organic semiconductor/metal- (metal/organic/metal)

As it was already mentioned, there are two counteracting factors that affect the electrical behaviour of the organic/metal contact: the motion of the metallic atoms through the organic film determining the penetration depth correlated with the Coulomb repulsion and the chemical reaction with the substituent group that limits the motion of the atoms. The

metal atoms diffusion stops when the saturation of the organic film takes place or when the front of molecules , which have not reacted, are too deep below the surface of the organic film.

As can be seen in Figure 6.7, the structure shows a characteristic close to ohmic for voltages between 1 V and 10 V. An exponential dependence between I and V , previously observed in m-DNB films doped with resorcinol, has been evidenced for PTCDA films at voltages < 1 V suggesting a Poole-Frenkel conduction mechanism (Stanculescu, 2006 b; Silveira, 2004) with a field dependent mobility of the charge carriers. At voltages > 10 V the effect of the space-charge limited current became significant.

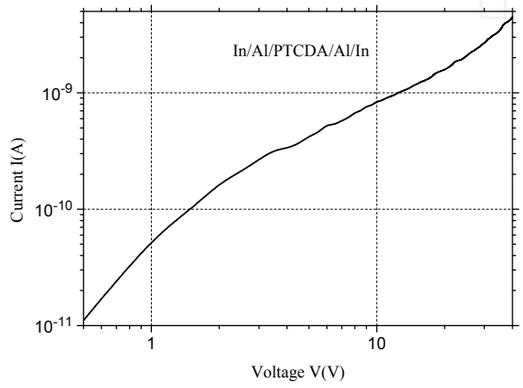


Fig. 6.7. I-V characteristic for Al/PTCDA/Al structure with planar grid electrodes (the contact with the electrodes was realised with In) (Stanculescu, 2007 a)

7. Organic heterostructures with buffer layer

A way to control the conduction properties through multilayer organic heterostructures is to introduce a buffer organic layer with special structural and energetical properties between the electrode and the first deposited organic layer. The quality of the initial organic layer deposited on a substrate can also be controlled by the morphology of this intermediate layer situated between the substrate and the organic layer being a way to minimize the influence of the deposition substrate.

A supplementary organic layer could facilitate the injection of the holes in the Si/organic/organic/Si structures, if the condition of a small difference between the ionisation energy of the supplementary organic layer and the valence band level in semiconductor (Si) is satisfied. The electrons injection could be facilitated in metal/organic/organic/Si structures for small differences between the work function of the metal and the electron affinity of the supplementary organic layer. The effect of the electrode can be eliminated using as contact electrodes the same type of Si wafers.

The injection of holes from the Si electrode to perylene or PTCDA could be improved with an intermediary organic layer having a higher level of the ionisation energy than perylene or PTCDA. An improvement in the injection of the charge carriers from Si to PTCDA has been obtained introducing an intermediate organic layer of ZnPc [IE=5.28 eV (Eastment, 1973); Eg=1.94 eV (Gao, 2003; Gao, 2001)] and generating a ZnPc/PTCDA, organic/organic heterojunction. The difference between the valence band energy in p type Si and the

ionisation energy is smaller for ZnPc than for PTCDA and therefore the intercalation of the ZnPc layer leads to a significant increase (more than one order of magnitude) in the current that passes through the Si/PTCDA/Si structure, as can be seen in Figure 7.1. No significant change has been observed in Figure 7.1 for the structure Si/ZnPc/perylene/Si because ZnPc and perylene have close ionisation energy.
The injection properties in the structure Cu/organic/n type Si, for a given polarization can be influenced by the introduction of an intermediate layer of ZnPc. Because the electron affinity of ZnPc (EA=3.34 eV) is lower than that of PTCDA (EA=4 eV), an intermediate layer of ZnPc is not significantly improving the electron injection from Cu cathode to PTCDA. The current has increased from 10^{-5} A to 3×10^{-4} A, for an applied voltage of 1 V. An increase in injection could be obtained at forward bias with an intermediate organic layer with an electron affinity lower than PTCDA.

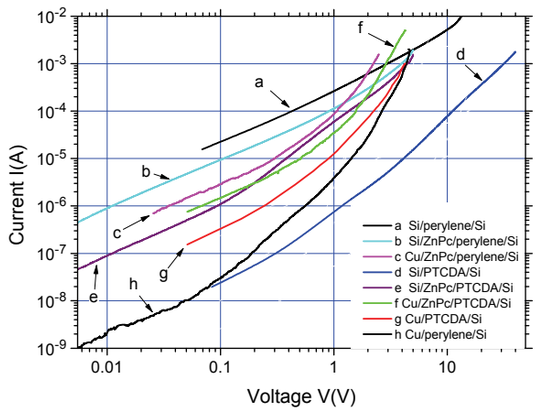


Fig. 7.1. The effect of the intermediate ZnPc layer on the I-V characteristics of the Si(Cu)/perylene (PTCDA)/Si heterostructures (Stanculescu, 2008)

Introducing a supplementary layer of ZnPc, for an applied voltage of 1 V, the current has increased from 8×10^{-7} A to 6×10^{-5} A in Si/PTCDA/Si heterostructure because the ionisation energy of ZnPc is situated between the hole energy in Si and the ionisation energy in PTCDA and favours the injection of the holes from p type Si to PTCDA.
A supplementary layer of ZnPc has not significantly influenced the conduction in the heterostructure Si/perylene/Si, because the ionisation energy of ZnPc and perylene have close value, 5.25 eV and 5.1 eV respectively. A significant increase in the electrons injection at forward bias in Cu/ZnPc/perylene/Si(p) structure is evidenced in Figure 7.1 and has been obtained because the difference between the work function of Cu and the electron affinity of the organic is smaller for ZnPc than for perylene. The current has increased from $3x10^{-6}$ A to 10^{-4} A, with ~ two orders of magnitude, for an applied voltage of 1 V.

8. SIS and MIS type structures on ITO substrate

The electrical conduction properties of different types of heterostructures realised on ITO/glass substrate, with single or multi organic layer and different types of metallic or p type Si contacts, at forward or reverse polarization, have been investigated. The electrode positively biased was name anode. High purity (5N) In was used to contact the electrodes.

The structures prepared with double organic layer, Alq3/PTCDA have shown similar behaviour revealed in Figure 8.1, for the same anode, Si(p)/In, and different cathodes (ITO/In; Al/In).
If the succession of the organic layer is changed from Alq3/PTCDA to PTCDA/Alq3 and if it is used the Al/In anode instead of Si(p)/In anode, no significant changes have appeared in the shape of the I-V characteristics presented in Figure 8.1, for voltages higher than 0.1 V. The only change is in the value of current. For an applied voltage of 1 V the highest current, $I=3x10^{-4}$ A ,was obtained in the structure consisting of a glass substrate, In contact, Al cathode, electron transporting layer Alq3, hole transporting layer PTCDA, Si(p) anode and In contact, In/Al/Alq3/PTCDA/Si(p)/In, presented in Figure 8.1.

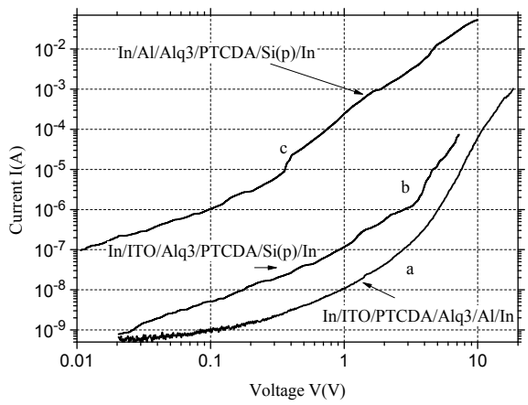


Fig. 8.1. I-V characteristics in double-organic layer structures: (Stanculescu, 2007 b)
(a) In/ITO/PTCDA/Alq3/Al/In;
(b) In/ITO/Alq3/PTCDA/Si(p)/In;
(c) In/Al/Alq3/PTCDA/Si(p)/In

In the structures ITO/organic/Si at reverse polarization (ITO is cathode), the barrier for holes is higher at the contact with α-NPD [IE=5.52 eV (Hirose, 1996), Eg=3.1 eV (Rajagopal, 1998)] compared to the contact with ZnPc [IE=5.28 eV (Gao, 2002), Eg=1.94 eV (Gao, 2001; Gao, 2003)]. In consequence, the injected current is two orders of magnitude lower in ITO/α-NPD/Si heterostructure than in ITO/ZnPc/Si heterostructure for voltages lower than 7 V, as it is presented in Figure 8.2.
This behaviour can be explained by the higher ionisation energy of α-NPD compared to ZnPc that determines better injection properties for the contact ITO/ZnPc compared to ITO/α-NPD.
Introducing a supplementary layer of perylene characterised by IE=5.1 eV (Kang, 2005) and Eg=2.5 eV (Kang, 2005) or PTCDA characterised by IE=6.8 eV (Rajagopal, 1998) and Eg=2.2 eV (Rajagopal, 1998), the current passing through the structure ITO/ZnPc/Si decreases from $I=2\times10^{-4}$ A to $I=3\times10^{-6}$ A in the structure with a supplementary layer of perylene, and from $I=2\times10^{-4}$ A to $I=6\times10^{-8}$ A in the structure with a supplementary layer of PTCDA, for an applied voltage of 1 V.
In Figure 8.2 can also be seen that, at voltages lower than 5 V the supplementary layer of α-NPD has as effect a decrease in the value of the current in the structure ITO/perylene/Si while the supplementary layer of ZnPc has as effect an increase in the value of the current.

This behaviour is determined by the height of the energetic barrier: $\Delta E_{\alpha\text{-NPD/perylene}}$=0.42 eV and $\Delta E_{ZnPc/perylene}$=0.18 eV. The current is predominantly a hole current resulting from the efficient hole injection from the low resistivity (6.7 Ωcm), p type Si anode.

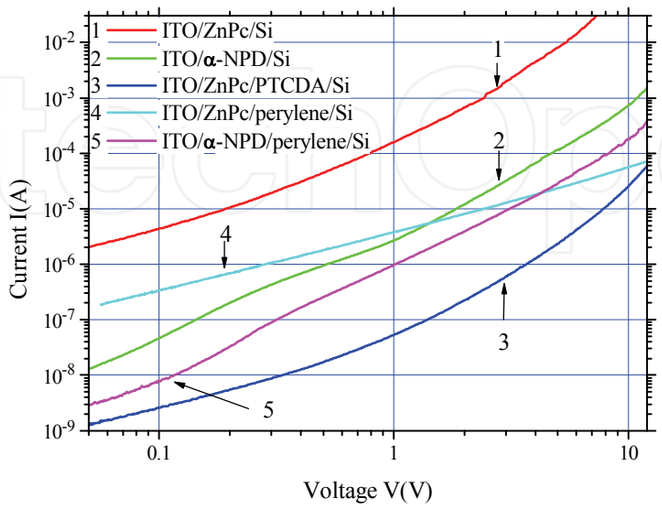


Fig. 8.2. I-V characteristics for ITO (Si)/single (double) p type organic thin film(s)/Si heterostructures (Rasoga, 2009):
1. ITO/ZnPc/Si(Cz, E/E, p: 0.018 Ωcm);
2. ITO/ α-NPD/Si(Cz, E/E, p: 0.64 Ωcm);
3. ITO/ZnPc/PTCDA/Si(Cz, E/E, p: 0.015 Ωcm);
4. ITO/ZnPc/perylene/Si(Cz, E/E, p: 0.014 Ωcm);
5. ITO/α-NPD/perylene/Si(Cz, E/E, p: 6.77 Ωcm)

9. Conclusion

The purpose of this chapter is to enlarge the knowledge about the electrical conduction processes in organic thin films and organic multilayer heterojunctions. The conduction properties of the following types of organic heterostructures have been analysed:

i. inorganic semiconductor [ITO, single silicon (Si)]/organic compound (Semiconductor/Insulator heterostructure=SI);
ii. organic compound/metal (Metal/Insulator heterostructure=MI);
iii. inorganic semiconductor (ITO, Si)/single (multi) organic layer(s)/metal, Si (Semiconductor/Insulator/Semiconductor heterostructure=SIS; Metal/Insulator/Semiconductor heterostructure=MIS);
iv. metal/organic layer/metal (Metal/Insulator/Metal structure=MIM).

Two basic processes are controlling the electrical transport reflected by the I-V characteristics in the inorganic semiconductor/organic/metal (semiconductor) heterostructures: (a) the injection of the charge carrier from electrodes into the semiconductor layer and (b) the transport of charge carriers in the bulk of the layer. The electrical transport is either injection limited by the energetic barrier at the interface or bulk transport limited by the low mobility of the charge carriers in organics (which usually is 2 or 3 orders of magnitude lower than in silicon) that induces a limitation associated with the

space charge and space charge limited currents (SCLC). The electrical conduction properties can also be determined by the defects (grain boundaries and imperfections) generated during the deposition in the organic films and acting as trap centres that induce a limitation associated with the trap charge and trap charge limited current (TCLC).
Therefore, charge carrier injection at the interface between metal and organic is more complicated than the charge carrier injection at the contact metal/inorganic because of the defects than can be induced in the organic layer during the deposition of the metallic contact.
The efficient injection of the holes into a p type conduction organic semiconductor is possible from an ITO semiconductor layer with an effective electrode work function higher than the ionization potential of the organic that favours an ohmic contact and the injection of the charge carriers from electrode to organic.
In this chapter have been presented some comparative investigations on the electrical properties of the interface inorganic/organic and organic/organic in different single and multi organic layer based structures and the electrical conduction through different types of heterojunctions {examples: ITO, Si/wide-gap n type or/and p type organic semiconductors [5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine synthetic (TPyP); tris(8-hydroxyquinoline) aluminium (Alq3) or/and zinc phthalocyanine (ZnPc); perylene; 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA), N,N'-di[(1-naphtalenyl)-N,N'-diaphenyl]-(1,1'-biphenyl)-4,4'-diamine (α-NPD); benzil, meta-dinitrobenzene (m-DNB)]/Si(Cu)}.
The effect of the types of electrodes, preparation conditions, succession order of the layers and molecular packing on electrical conduction in organic compound based heterostructures have been analysed.

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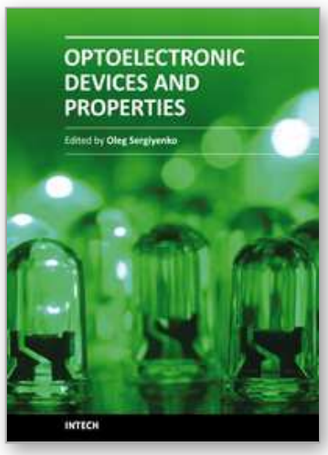
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