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Charge carrier transport phenomena in some organic heterojunctions

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This paper presents investigations on the electrical transport phenomena in sandwich type inorganic/single (double) organic layer/inorganic such as silicon; ITO/TPyP, Alq3, α-NPD; ZnPc; perylene; PTCDA/silicon and inorganic (metal)/organic/metal such as silicon (Al)/ZnPc; α-NPD; TPyP/copper, Al, structures, prepared by vacuum evaporation. For most of these heterostructures the I-V characteristics in the static regime have a near ohmic behaviour only at low voltages (<1 V) that changes in a power dependence with a coefficient n=2 or n=3 at higher voltages because of the space charge or trapped charge phenomena. For the same applied voltage, the n type Si electrode injects more charge carriers in TpyP than in Alq3. For higher voltages (>10V) an increased number of charge carriers are injected from n type Si in Alq3 compared to TpyP. The injection properties of the interface ITO, Cu, Al electrode/organic layer have also been investigated. The best injection has been obtained through ITO/ZnPc interface. For a grid configuration of the Al electrodes the transport phenomena are determined by the resistivity of the structure.

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1. Introduction

The crystalline organic semiconductors are a class of materials with special properties offering the perspective of a large field of experimental applications and theoretical studies. The extended π-electron systems and their interaction in the organic materials with low molecular weight (small molecules) are determinant for the electronic and optoelectronic properties of these materials. This increased interest is justified by the large variety of organic compounds and their special properties that make them adequate for organic light emitting diodes (OLED) [1], solar cells (OPV) [2], photodetectors [3] and organic field effect transistor (OFET) [4], leading to applications such as: organic/bioorganic sensors, very cheap organic circuits that operate at low switching voltages corresponding to cost restrictions and organic active matrix drivers for the complementary organic display technology. The organic devices are interesting because their fabrication processes are less expensive and complicated than that of the Si based devices and because their technology is anticipated to be compatible and complementary with the silicon VLSI technology. Organic semiconductor material is the most important component of the organic field-effect transistor (OFET) and the metal-organic contact induces the most serious limitation of the OFET performances. The inorganic (semiconductor, metal)/organic junction as the key element of any organic device can offer the possibility to overcome the disadvantages of the conventional inorganic heterostructures, but the injection process of the charge carriers across the interfaces of the structure and the transport of the hole and electrons inside the devices influence the performances of the organic devices. For example, a high resistance of the inorganic/organic contact generates drops of the externally applied drain voltage across the metal/organic contact and not across the transistor channel and introduces the most serious limitation of the field effect transistor operation such as reduced drain saturation current and longer switching times [5]. It can also cause the loss of energy in the device and, by heating, the degradation of the organic material making the device impractical to operate and limiting its lifetime. This undesired voltage drop could be reduced by an ohmic behaviour of the inorganic/organic semiconductor contact.

The improvement of the electronic transport properties of the inorganic/organic interface will lead to the lowering of the operating voltage and, as consequence, to the reduction in power consumption of the devices.

The electrical transport properties are determined by the low mobility of the charge carrier 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 trapped charge. Because of these limitations the circuits prepared with organic materials are lower speed circuits.

This paper presents some comparative investigations of the electrical transport phenomena at the interface inorganic/organic and organic/inorganic, in different single and multi-organic layer based structures: Si; ITO; Cu, Al/wide-gap “n” or/and “p” organic semiconductors [5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine synthetic (TPyP); tris(8-hydroxyquinoline) aluminium (Alq3) or/and zinc phthalocyanine (ZnPc); N,N’-di-[(1-naphtalenyl)-N,N’-diaphenyl]-(1,1’-biphenyl)-4,4’-diamine (α-NPD); perylene; 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA)]/Si; Al. We have studied the injection properties through these heterojunctions and the effect of the type of substrates, preparation conditions and succession order of the layers on the transport properties of the carriers.

2. Experimental

To investigate the electrical conduction properties of the interface inorganic/organic and organic/organic in double layer structures, and draw the I-V plots we have prepared sandwich type Si; ITO (Aldrich)/”p”; “n” organic (Aldrich)/Si (SIS); Cu, Al/”p”; “n” organic/Si, Al (MIS; MIM) structures in a process in two steps. Firstly we have manufactured the inorganic/organic (SI) and metal/organic (MI) junctions and subsequently the SIS and MIS structures putting into direct contact the organic films of two (SI) and, one (SI) and one (MI) individual junctions [6,7]. In SIS and MIS structures we have used as inorganic semiconductor electrode etched/etched (E/E) single crystal silicon wafers with different type of conductivity (“p” or “n”) and resistivity (8×10^{-6}-7 Ωcm), ITO covered aluminosilicate glass slide (5-15 Ω/sq and as metallic electrode copper films deposited on textolite substrate.

Single silicon (Si) could be used as an ohmic charge injection contact for organic materials of high ionization potential because of its promising properties such as the high mobility of the charge carriers, the possibility to be “p” and “n” doped and to the reduced surface reactivity and interfacial interactions obtained by chemical processing (etching). The effect of the charge and defects states at the interface on the charge transport mechanism is important for the optimisation of the devices from the point of view of the efficiency, temporal response and long-term stability.

To prepare the MIM structures we have deposited by vacuum evaporation method the aluminium electrodes with a special grid type configuration [6].

We have prepared stable, homogeneous films with a rectangular geometry and a good adhesion to the substrate (film thickness 20-100 nm [8]) by vacuum evaporation and deposition using an Alcatel system with turbomolecular pump ($<1.5\times10^{-5}$ mbar). Preliminary results about the experimental parameters affecting the quality of the film have been previously presented [8]. We have improved the evaporation system using a self-sustainable kanthal winding and a quartz crucible in a special configuration to generate and control a directional flux of molecules towards the support sustaining the deposition substrates (Si wafers successively cleaned ultrasonically, with acetone, hydrofluoric acid and distillate water; Al and Cu layers successively cleaned with diluted solution of nitric acid and distillate water and ITO/glass cleaned with acetone).

We have investigated the electrical conduction in these heterojunctions using a typical 2 points perpendicular contact geometry, which is sensible both to the influence of the contacts between the measure probes and the inorganic electrodes and to the presence of the barriers at the interfaces across the structure. The current-voltage (I-V) curves have been recorded with a computer assisted Keithley 2400 Sourcemeter. The resistivity of the silicon wafers has been measured using the standard in-line four-point probes configuration.

3. Results and discussion

The I-V characteristics of the SIS, MIS and MIM prepared structures have been plotted in the static regime and large voltage range (0.01-20 V with extension to 40 V and 100 V) using reverse polarised experimental structures with ITO negatively biased and Cu positively biased. As an alternative to optimise the charge transport in the organic materials, reducing the grain boundaries, imperfections and traps having a limiting effect [7], we have tried to obtain high order molecular organic thin films selecting the organic compound, the electrodes and the preparation method. The deposition substrates (Si, ITO/glass, Cu/textolite, Al/glass) have influenced the arrangement of the organic molecules and the quality of the organic film. The transport process in these heterostructures is determined by the properties of the silicon wafers. We have selected for deposition a Si (E/E) wafer because the chemically polished Si surface ensures a better injection of the charge carriers compared to only lapped mechanically polished (L/L) Si surface, the electrical mechanically damaged surface introducing a higher disorder in the organic layer and lowering the electrical conduction.

The standard test method with in-line four-point probes [7] has been utilized to calculate the resistivity of the silicon single crystal wafers:

$$\delta = R_m \times F \times w \qquad (1)$$

where δ(Ωcm)=resistivity of specimen at room temperature, R_m(Ω)=average resistance [7], F=geometrical correction factor= 4.507 [7] and w(cm)=specimen thickness.

The organic thin film situated between two contact materials shows a I-V curve that deviates from the ohmic behaviour. For high value of the electrical field, the electrical conduction in the organic junctions is influenced by the accumulation of the charge carriers as space charge that generates a limitation of the current. This is caused by the energetic barriers (associated with the molecular energetic levels of the selected organics), by the mobility barriers at the interface (due to differences in the charge carriers mobility) and by the field dependence of the charge mobility.

An alternate procedure to optimise the charge transport in organic materials is offered by the molecular order in the organic solid state of conjugated systems. In the studied compounds the carrier transport is based on the free electron of the aromatic system and could be improved by the overlap between the adjacent molecules in the organic solid state that favours the superposition of the aromatic rings [9,10].

The general shapes of the I-V curves are not very different for “n” type Si/TPyP or “n” type Si/Alq3 but the current is less than one order of magnitude higher in “n” Si/TPyP structure at applied voltages <1 V. For an applied voltage of 1 V the interface between “n” Si wafer and “n” conduction organic (TPyP; Alq3) (Figure 1) presents a much higher injection of the charge carriers ($J_{TPyP}=1.5\times10^{-7}$ A; $J_{Alq3}=2.5\times10^{-8}$ A) than the interface between “p” Si wafer and the same “n” type conduction organic ($J_{TPyP}=2.5$ ligands 10^{-11} A). On the other hand the behaviour of the organic/inorganic semiconductor interface is also caused by the preferential adsorption of the organic molecules on the defect site of the surface. The packing of the organic layer is controlled by intermolecular interactions while the coupling to the substrate induces the orientation of the organic layer [11]. Therefore, the molecular conformation of the species adsorbed on the substrate is very important and the lateral ligands ensure a higher conformational mobility and a good conformational adaptation to the surface of the “n” Si substrate for Alq3 and TPyP.

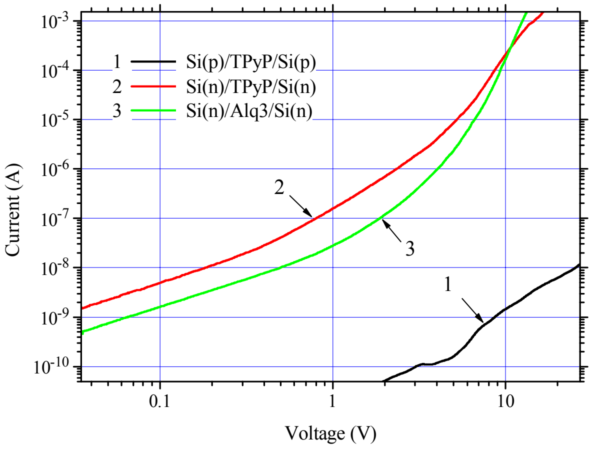

Fig. 1. I-V characteristics for SIS structures based on single „n” type organic thin film: 1. Si(Cz,E/E,p; 1.34 Ωcm)/TPyP/Si(Cz,E/E,p;1.34 Ωcm); 2. Si(Cz,E/E,n;0.008 Ωcm)/TPyP/Si(Cz,E/E,n;0.008 Ωcm); Si(Cz,E/E,n;0.008 Ωcm)/Alq3/Si(Cz,E/E,n; 0.008 Ωcm).

The injection at the interface “n” Si and “n” organic (Figure 1) is lower than the injection at the interface between “p” Si wafer and “p” conduction organic ZnPc ($J_{ZnPc}=7\times10^{-4}$ A at 1 V applied voltage) because of the lower efficiency of the coupling between the substrate and the π-electrons system of the organic (Figure 2).

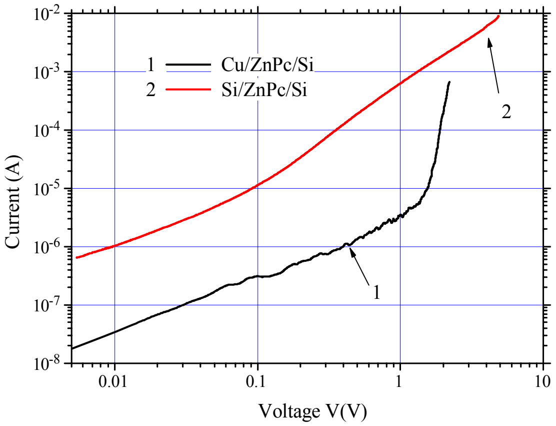

Fig. 2. I-V characteristics for inorganic semiconductor (metal)/ZnPc/Si structures: 1. Cu/ZnPc/Si (Cz,E/E,p;0.018 Ωcm); 2. Si(Cz,E/E,p;0.018 Ωcm)/ZnPc/Si (Cz,E/E,p;0.018 Ωcm).

The number of charge carriers injected is higher in “p” type Si/ZnPc structure because ZnPc (as well as PTCDA) is a planar aromatic molecule characterized by a preferred orientation of the molecular planes and small intermolecular plan distances [12,13] that ensures a significant overlapping between the π-electrons clouds of neighbouring molecules, a higher mobility of the charge carrier and a good conduction.

A high value of the current (10^{-2} A at 4 V applied voltage) was obtained through a sandwich type structure: ZnPc films between two silicon wafers (“p” type, E/E, low resistivity: 0.018 Ωcm) (Figure 2). The deviation from the linear I-V dependence due to the low mobility and space-charge limited currents is not so important in ZnPc because the charge is easier transmitted from a molecule to another through the closed molecular stacking.

The current is higher for voltages <1 V, in Si/ZnPc/Si heterostructure (7×10^{-7} -7×10^{-4} A; Figure 2, curve 2) compared to Cu/ZnPc/Si heterostructure (2×10^{-8}- 4×10^{-6} A; Fig. 2, curve 1).

At forward bias the injection properties depend on the energetic barrier between the work function of copper (Φ_{Cu}=4.5 eV [22]) and electron affinity of ZnPc (EA=3.34 eV) is ΔE=1.16 eV.

At reverse bias, Cu anode, (Fig. 2, curve 1) the conduction is favoured by the low energetic barrier $\Delta E_{Si/ZnPc}$=0.18 eV that sustains the hole “absorption” from the low resistivity 0.018 Ωcm “p” type Si substrate.

An electrical breakdown mechanism (Fig. 2, curve 1) was evidenced in Cu/ZnPc/Si structure at voltages >2 V, due to the metallic film quality correlated with the presence of the defects and/or contaminants on the Cu electrode. The quality of the electrochemically deposited Cu layer is low and an oxide layer covers the metal. Another potential cause for the breakdown of the structure could be the damage of the organic film during the preparation.

The defects are generated during the deposition process (Cu electrode was deposited electrochemically and not by vacuum evaporation) and the contaminants with the oxide layer.

Theoretically, the injection properties of the contacts are determined by comparing the energy of the holes in the valence band of the p type silicon (E_V~5.1 eV) with the energy of the HOMO level of the organic compound or the energy of the electrons in the conduction band of "n" type silicon (E_c~4 eV) with the energy of the LUMO level of the organic compound. A higher injection of electrons was obtained from "n" type silicon in TPyP (E_{LUMO}~4.1 eV [14]) compared to Alq3 (E_{LUMO}=3.25 eV [15]) and it 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 conduction band level in "n" Si and the electron affinity level is higher in Alq3 (ΔE~0.75 eV) compared to TPyP (ΔE~0.10 eV).

The I-V plots are generally symmetric for perylene derivative (PTCDA) with respect to the current direction (Fig. 3). This is due to the fact that the non-linear I-V dependence favoured by the low mobility of the charge carriers in organic solids that generate space-charge limited currents is not so important and the electron is easier transmitted from a molecule to another through the closed molecular stacking in a direction perpendicular to the film.

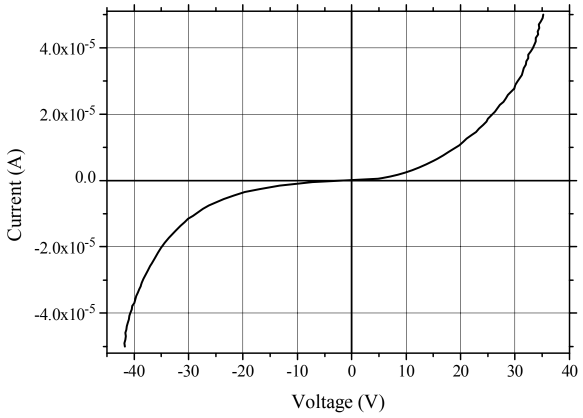

Fig. 3. I-V characteristic for perylene based SIS structure Si(Cz,E/E,p;1.34 Ωcm)/perylene/Si (Cz,E/E,p;1.34 Ωcm).

The contact between the two PTCDA layers has no influence on the shape of the I-V plots. This fact is supported by the I-V characteristics plotted before and after the destruction and subsequent recovering of the contact (Fig. 4).

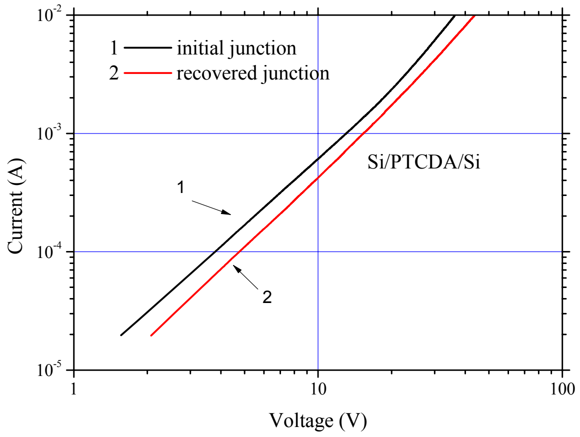

Fig. 4. I-V characteristic for SIS PTCDA based SIS structure Si(Fz,L/L,n;51 Ωcm)/PTCDA/Si (Fz,L/L,n;51 Ωcm).

The behaviour of the interface organic/organic has a significant influence on the shape of the I-V plots by the charge accumulation process (Fig. 5 and Fig. 6).

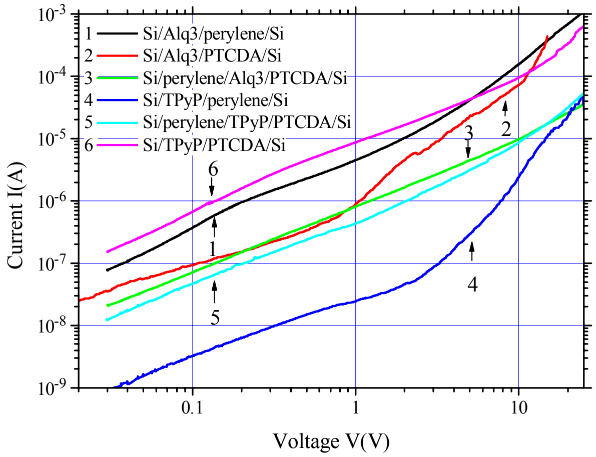

Fig. 5. I-V characteristics for SIS structures based on double „n-p" organic thin films:
1. Si(Cz,E/E, n;0.008 Ωcm)/Alq3/perylene/Si(Cz,E/E,p; 6.78 Ωcm);
2. Si(Cz,E/E,n;0.008 Ωcm)/Alq3/PTCDA/Si(Cz,E/E,p; 1.34 Ωcm);
3. Si(Cz,E/E,p;1.34Ωcm)/ perylene/Alq3/PTCDA/ Si(Cz,E/E,p,6.78 Ωcm);
4. (Cz,E/E,n,0.008Ωcm)/TPyP/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

For structures with double organic layer, "n" (TPyP or Alq3)-"p" (PTCDA or perylene) at reverse polarization and an applied voltage of 1 V (Figure 5), the highest current was obtained in Si/TPyP/PTCDA/Si (J=9×10^{-6} A) and Si/Alq3/perylene/Si ($J=3.5\times10^{-6}$ A) structures. We consider the energetic barriers for hole at the n-p junctions resulting from the value of the ionisation energy for each organic compounds: $\Delta E_{TPyP/PTCDA}\sim0$ eV; $\Delta E_{Alq3/PTCDA}=0.85$eV; $\Delta E_{TPyP/perylene}=1.7$ eV; $\Delta E_{Alq3/perylene}=0.85$ eV. (The position of the HOMO level in TPyP was estimated from the LUMO position (EA=4.1 eV) and the optical band gap ($E_g=2.7$ eV) evaluated from the transmission spectra of TPyP thin films). The energetic levels in silicon for the valence band assimilated with HOMO in organics and conduction band assimilated with LUMO in organics are $E_{VB}=5.1$ eV and $E_{CB}=4$ eV.

For the structures with triple organic layer perylene/Alq3 (TPyP)/PTCDA the currents are slightly different at reverse polarization (Figure 5). The supplementary perylene layer decreases the current at 1 V applied voltage in the Si/TPyP/PTCDA/Si structure with one order of magnitude because of the high energetic barrier at the contact perylene/TPyP ($\Delta E=1.7$ eV). No significant influence of the supplementary perylene layer on the current in Si/Alq3/PTCDA/Si structure has been evidenced at voltages <1 V. The effect of the energetic barrier at the contact perylene/Alq3 ($\Delta E=0.85$ eV) becomes significant at voltages 10V.

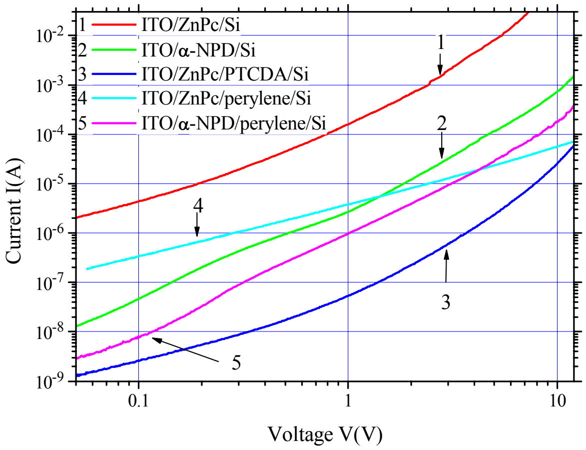

Fig. 6. I-V characteristics for ITO(Si)/single (double) "p" organic thin film(s)/Si structures: 1. ITO/ZnPc/ Si(Cz,E/E,p;0.018 Ωcm); 2. ITO/α-NPD/Si(Cz,E/E,p;0.64 Ωcm); 3. ITO/ZnPc/PTCDA/ Si(Cz,E/E,p;0.015 Ωcm); 4. ITO/ZnPc/perylene/Si (Cz, E/E,p;0.014 Ωcm); 5. ITO/ α-NPD/perylene/Si (Cz,E/E,p;6.77 Ωcm);

In ITO/organic/Si structures, at reverse bias (ITO cathode), the barrier for hole is higher in α-NPD (IE=5.52 eV [19], $E_g=3.1$ eV [15]) compared to ZnPc (IE=5.28 eV [16], $E_g=1.94$ eV [17,18], because α-NPD has a higher ionisation energy than ZnPc and the ITO/ZnPc contact presents better conduction properties than ITO/α-NPD (Fig. 6).

Introducing a supplementary perylene (IE=5.1 eV [20], $E_g=2.5$ eV [20]) or PTCDA (IE=6.8 eV [15], $E_g=2.2$ eV [15]) layer the current through ITO/ZnPc/Si structure decreases from 2×10^{-4} A to 2×10^{-6} A (perylene) respectively 6×10^{-8} A (PTCDA). At voltage <4 V a the α-NPD layer decreases the current in the structure ITO/perylene/Si compared to ZnPc layer because of the energetic barriers: $\Delta E_{\alpha\text{-NPD/perylene}}=0.42$ eV and $\Delta E_{ZnPc/perylene}=0.18$ eV.

The current is predominately a hole current that results from the efficiency of the hole injection from the low resistivity (6.7 Ωcm), p type Si anode (Figure 6).

The carrier injection mechanisms at the interfaces metal/organic molecular solid having π-conjugated systems are more complex than at the metal/inorganic semiconductor interface because of the same space-charge limitation effects mechanism that can obscure the real contact properties [21]. The temperature is high during the deposition of a metal on the organic, the layer is affected and more defects are created on the organic surface. As a consequence we have chosen to deposit the molecular layer onto the Cu and Al electrode in a reverse succession of the deposition stages. The temperature involved by organic film deposition (<300 ºC) couldn't damage the metallic layer and the defects generated at the interface have become less significant. The order of the preparation of the films is not important in organic/organic heterojunction because the system is not submitted to high thermal variation.

The shape of the I-V characteristics of the Al/ZnPc /Al, Al/α-NPD/Al and Al/TPyP/Al (Figure 7) grid structures was determined by the low value of the electric field for the planar configuration of the anode and cathode contacts compared to a sandwich structure ($E\sim10^{3}$ V/m respectively $E\geq10^{6}$ V/m at 1 V applied voltage). These structures have shown ohmic characteristics at voltages between 0.8 V and 10 V. This behaviour is similar with those of Al/PTCDA/Al structure previously mentioned [6].

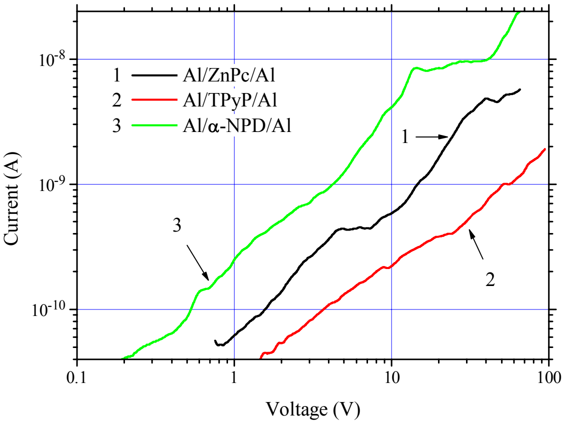

Fig. 7. I-V characteristics for MIM structures based on "p" or "n" type organic with Al grid electrode: 1. Al/ZnPc/ Al; 2. Al/TpyP/Al; 3. Al/α-NPD/Al.

The number of the charge carriers injected from the Al electrode is higher in α-NPD and ZnPc compared to TPyP despite the metal/organic energetic barrier. This behaviour can be explained by the configuration of the electrode. The grid configuration of the electrodes implies a bulk process in the organic layer and it is correlated with the resistivity of the structure, while the sandwich type structure implies an energetic barrier at the interface.

4. Conclusions

The I-V plots of silicon/organic/silicon, SIS and silicon (metal)/organic/metal MIS (MIM) heterojunctions and the effect of the organic/inorganic and organic/organic contacts depending on the substrate properties, organic compound properties and deposition conditions have been studied. For most of the prepared heterostructures we have emphasised a dominant ohmic behaviour at low voltages (<1 V) and the appearance of the space charge effect at higher voltages. A reduced effect of the space charge limited currents has been observed in ZnPc because of the special crystallization particularities of these aromatic compounds. The injection/transport properties at the Si/TPyP interface are better than those at Si/Alq3 interface for “n” type silicon electrodes. In reversed biased ITO/ZnPc/Si structure the charge transport is better than in ITO/α-NPD/Si structure because of the efficient injection of holes from the low resistivity Si anode. A good conduction has been emphasised in the Cu/”p” organic/Si structure even at reverse bias due to the hole “absorption” from the “p” type Si substrate because of the low energetic barrier at the contact “p” Si/organic.

Acknowledgements

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