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Effect of the metallic contact on the electrical properties of organic semiconductor film

F. STANCULESCU*, A. STANCULESCU[a], M. SOCOL[a]
University of Bucharest, Faculty of Physics, 405 Atomistilor Street, P.O.Box MG-11, Magurele, Bucharest, 077125 Romania
[a]*National Institute for Materials Physics, 105bis Atomistilor Street, P.O.Box MG 7, 077125 Magurele, Bucharest, Romania*

Sandwich type (MIS) heterostructures based on layers of organic semiconductors as meta-dinitrobenzene (m-DNB) and perylene or perylene derivative 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) have been prepared using alternative methods (rapid thermal directional solidification or two-steps, vacuum evaporation and deposition process) on different substrates (single crystal silicon wafer and textolite covered with copper film). Subsequently indium, gallium, aluminium of high purity (5N) and silver have been used for the preparations of the metallic contacts. This paper presents some investigations of the contact between different organic semiconductors and several metals: meta-dinitrobenzene/Cu, perylene/In, perylene/Al, perylene/Ga, perylene/Ag, PTCDA/Al, PTCDA/Ga, and PTCDA/Ag. The comparative study of the electrical conduction properties of these organic semiconductor/metal contacts has emphasised significant differences depending on the metal type, metal/organic semiconductor interface properties and quality of the contact, which is determined by the preparation method (pressing, melting, vacuum evaporation, painting) and selected contact configuration. The experimental data obtained using the 2 points contact geometry have evidenced linear or power I-V dependences of the investigated metallic contacts emphasising the importance of the space-charge phenomenon and defects on the charge carriers' transport in these structures.

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1. Introduction

Molecular materials were considered in the last decade a very important alternative to the inorganic semiconductors in the manufacturing of electronic [1-14] and opto-electronic [15-23] devices because of the large variety of organic compounds, their special properties and low production cost compared to inorganic semiconductor.

The performances of organic devices are influenced by the process of charge carriers' injection at the metal/organic semiconductor contact and are determined by the stability and resistivity of the contacts. For the operation of organic electronic devices the injection of the charge carriers from the metal to the π conjugated system is very important [24].

Charge carriers injection at interface between metal and organic is more complicated than in metal/inorganic contacts because in this case the contact properties can be influenced by the defects induced on the organic surface by the metallic contact and the space-charge effect characterizing the organic semiconductors.

High efficiencies, low working voltages and long lifetime of the devices involve contacts with low electrical resistivity and good chemical stability [24].

An integral part of the electrical measurements is the making of the metallic contact on the organic sample: the identification of the adequate metal and the preparation of the contact. The first requirement for good electrical contact is good physical contact between organic semiconductor and metal layers as pressed, melted, painted or evaporated contacts, each showing advantages and disadvantages.

For melted contact a heated foil (piece) or a small quantity of the selected metal is pressed onto the organic semiconductor determining the surface layer melting and solidification and inducing a disorder in the organic layer under the metallic contact [25].

For painted contacts as silver paste the most important problems are associated with the contamination and perturbation of the crystalline order of the organic layer [25].

Although the vacuum deposition method seems to be the best because of the good physical contact, lake of contamination or recrystallisation of the boundary layer, the vapour pressure of the organic material can induce a limitation and should not exceed 10^{-3} mm of Hg at room temperature [25].

Despite the importance of the contacts and heterostructures in organic/inorganic structures, a little attention was focussed on the investigation of chemical, electronic and structural organic/metal interface and as a consequence the study of the metal contacts and injection mechanisms in organic molecular crystalline materials are of great interest.

When the physical contact between metal and organic molecular solid is realized interface states are induced by metallization or interdiffusion [26]. The study of organic film/metal contact is important for injection mechanism, contact degradation, and the effect on the device performances.

Using a classical Schottky model of the metal/semiconductor contact [26] it is possible to assume that the barrier height depends especially on the metal work function [27] that offers a rough selection criteria of metals for opto-electronic applications. In consequence, for organic light emitting devices (OLED), as electron injector has to be used a metal characterised by a low work function [15]. Previously studies have mentioned In (work function=4.12 eV [26]) and Al (work function=4.25 eV [26]) as the most adequate metals for PTCDA contacting.

This paper presents a study of some organic semiconductor/metal contacts as meta-dinitrobenzene /Cu, /perylene/In; Al; Ga; Ag and PTCDA/Al; Ga; Ag prepared by different methods.

2. Experimental methods

To investigate the electrical conduction properties of crystalline organic semiconductor/metal contact we have firstly prepared sandwich type silicon/m-DNB/Cu, silicon/PTCDA/In, silicon/perylene (PTCDA)/Al, silicon/perylene (PTCDA)/Ag, silicon/perylene (PTCDA)/Ga heterostructures. To prepare the samples we have used as substrates single crystal silicon wafers very well characterised from the point of view of resistivity class, type of conductivity (“p” or “n”) and degree of surface processing (lapped, etched) and textolite platelets covered with a film of Cu.

For electrical measurements we have used: indium contact realized on silicon by local melting and on copper by pressing, liquid gallium contact and silver contact realized by painting silver paste.

Anisotropic m-DNB films have been prepared by a rapid thermal directional solidification method in dendritic growth conditions [28-30] between two substrates of the types mentioned above (etched/etched, low resistivity, “p” conduction single crystal silicon wafer and textolite covered with Cu). We have used either organic material powder or crystalline fragments from the ingots obtained by repeated melting zone purification or melt Bridgman crystal growth processes [31-34].

We have prepared stable, homogeneous films of perylene and perylene derivative (PTCDA) with a specified geometry and a good adhesion to the substrate in a vacuum evaporation and deposition process [35].

Perylene and PTCDA supplied by Aldrich were used without further purifications. Details about the most important experimental parameters affecting the quality of the films as the vacuum level ($<10^{-2}$Pa), evaporator geometry, evaporation temperature, deposition duration and specific geometrical configuration are presented in [35]. The evaporator has a special configuration to generate and control a directional flux of molecules towards the support sustaining the deposition substrates. A cylindrical glass shield to control the thermal regime and the flux of molecules surrounds this evaporator. The temperature during the evaporation stage was between 130-150 ^{o}C for perylene and 240-260^{o}C for PTCDA and the deposition duration of 5-10 minutes for both perylene and PTCDA.

We have investigated four types of metals for contacting the mentioned organic semiconductor: Cu (thin layer deposited on insulated textolite substrate) in contact with m-DNB; In and Al pressed on the organic layer (perylene and PTCDA), Ag paste painted on organic layer (perylene and PTCDA) and Ga melted on the organic layer (perylene and PTCDA). We have used high purity (5N) In, Al and Ga to reduce the tendency to oxidation of the metal, which can affect the quality of the contact.

Al and Ga metallic contact on organic semiconductor film (perylene, PTCDA) have been prepared using an intermediate thin insulating layer of Mylar [36] to avoid the short-circuit inside the structures.

To plot the I-V characteristics of these heterostructures we have used a typical 2 points contact geometry [37] frequently used in electronic devices properties investigations in an experimental set-up with computer assisted Keithley 2400 SourceMeter. The disadvantages of this method are the sensitivity to the nature of contacts and to the quality of barriers between the different layers of the structures, but the most important measurement difficulties are associated with very low values of the currents in these materials.

3. Results and discussion

Charge carriers transport model in aromatic compounds is based on the free electron gas of the delocalised π system of electrons but in the molecular plane this transport is impeded by the large distance between adjacent molecules and by the polar bonding of the hydrogen and oxygen atoms. The transport is very efficient in a direction perpendicular to the film surface along to the molecular stacks because of the lower intermolecular distance [38,39]. The π systems of different molecules are in contact and carriers can be easily transferred from one molecule to the other.

The order of the layers’ deposition stages (metal/organic or organic/metal) in the manufacturing of the heterostructures can be very important for the electrical behaviour [24,40]. When the organic layer is deposited on a metallic film appears the chemisorption of the organic molecules in determined sites controlled by the extended π-ring system irrespective of functional groups. When a metal is deposited onto an organic substrate may occur an important modification of the interface as a result of chemical reaction of the metal with organic molecules and/or diffusion of a large number of metallic atoms onto the organic layer, generating a high density of states in the organic semiconductor band gap [24].

The diffusion into the organic layer depends on the metal type and plays an important role in the electrical behaviour of the metal/organic interface. The main difference between different metals is generated by the degree of diffusion of the metal atoms in the organic film. The diffusion depends on the reactivity of the metal atom with the organic compounds and the reactivity of the molecule is highly dependent on the molecular structure.

So the substituent group to the aromatic nucleus as the end groups for PTCDA controls the interaction of the metal with organic molecules.

The PTCDA films consist in well-ordered stacks of molecules with the molecular plane parallel to the substrate surface and spaced by 3.21 Å [41]. This dimension is large compared to the atomic and respectively ionic radius of In (2 Å respectively 0.81 Å), Al (1.82 Å respectively 0.535 Å), Ga (1.81 Å respectively 0.62 Å), Cu (1.57 Å respectively 0.73 Å) and Ag (1.75 Å respectively 1.26 Å) that assures a natural path for motion of metallic atom/ion in the crystalline layer. The motion of the metal atoms is also facilitated by the local deformation of the organic crystalline lattice characterised by weak van der Waals bonds [26]. The quality of the film reflected in the presence of defects, as grain boundaries, can influence the motion of the metal atoms.

Indium and aluminium are very reactive with PTCDA and leads to the formation of a mixed interface layer through the oxidation of the deposited metal. There is a strong interaction between In, Al and anhydride group generating either In, Al attachment to the molecule or In-oxide or Al-oxide detachment from the molecule, the perylene core maintaining its original structure.

The chemical reaction between In and Al and PTCDA predominantly involves 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. Heat of formation of the reactive metals oxides is orders higher ($\Delta H_{298}=-1676$ KJ/mol for Al_2O_3, ($\Delta H_{298}=-1080$ kJ/mol for Ga_2O_3 and $\Delta H_{298}=-926$ KJ/mol for In_2O_3) than that characterising the noble metals ($\Delta H_{298}=-31$ KJ/mol for Ag_2O) and is higher than that for ordinary metals and justify the generation of the oxide in the detriment of metal-metal bonding.

The attachment of the electronegative anhydride groups to the perylene core causes the increase of the ionisation potential of perylene (IE=5.1 eV [26]). PTCDA has higher ionisation energy (IE=6.2 eV [26]) and electron affinity (EA) and its contacts with metals are characterized by negative charge (electron) transfer from metal (In, Al, Ga, Ag) to organic molecule [24].

The I-V characteristics deduced for the contact PTCDA/In [42] were explained by the "hopping" and tunnelling phenomena through the electronic states induced by the chemical reactions in the band gap of PTCDA. The high diffusion rate of In in PTCDA is associated with the ionisation of the In atoms generating ion-ion repulsion that prevent the clustering of the atoms in the layer or at the metal/organic interface and any surface accumulation. The metallization of the surface can be observed after the saturation of the organic film with metal atoms [43].

For PTCDA/Al contact we have emphasised an ohmic behaviour (Fig. 1) for low voltages (<0.3 V). Even the reactivity of Al with perylene is not significant (no substituent groups to the aromatic nuclei) it also diffuse through the perylene film characterized by a 3.46 Å separation between the parallel plans of the molecules [42]. For voltages >0.3 V we have emphasised a transition to a region characterised by a power dependence with an exponent n=2 associated with the presence of the space charge limited currents (SCLC).

The I-V characteristics of the perylene/Al contact (Fig. 2) are not linear at low voltages, but tend to an ohmic behaviour through weak supralinear dependence for direct bias. For reverse bias the I-V characteristics are weak sublinear. At very low voltages (< 0.03 V) the behaviour of this contact is ohmic. We have evidenced for direct bias a region characterised by a power dependence with an exponent n=2 at ~ 1 V. The same region is present for reverse bias but is shifted through ~ 10 V.

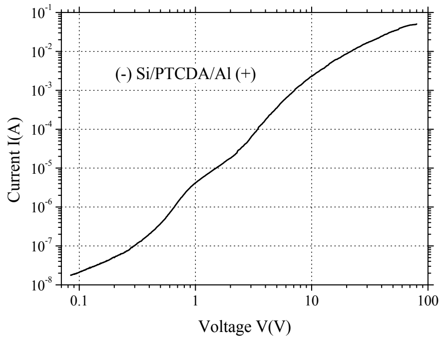

Fig. 1. I-V plot of silicon/PTCDA/Al heterostructure.

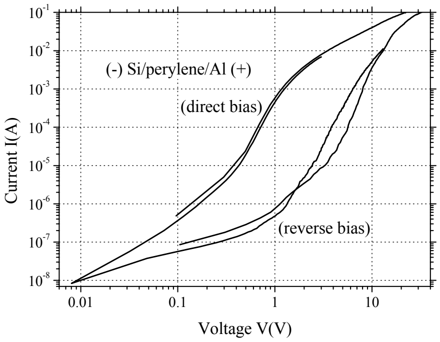

Fig. 2. I-V plot of silicon/perylene/Al heterostructure.

For perylene/In contact (Fig. 3), the reactivity of In is very weak but the diffusion of In is significant and induces states under the Fermi level. The ohmic character associated with carrier's injection mechanism of the perylene/In contact at low voltages (5 V for reverse bias and 2 V for direct bias) can be explained by the conduction associated with these states in the band gap in the interface region, just below the Fermi level [42]. At high voltages (>10 V for negative voltages) an exponential behaviour is dominant suggesting a transport mechanism by hopping.

The carriers tunnelling and hopping across the interface organic/metal is favoured by the states generated in the band gap by the diffusion and/or reaction taking place at the PTCDA(perylene)/Al(In) interface [26].

Disassembling these structures we have remarked that perylene film is not contaminated with Al, but Al remains on PTCDA film that prove a stronger chemical reactivity of PTCDA than perylene with metals.

The I-V characteristics of the PTCDA/Ag contact (Fig. 4) are ohmic only at low voltages (<0.1 V) because the reactivity of silver is reduced and does not induce enough interface gap states to be involved in the conduction process, and the space charge limited current phenomenon (n=2) become important at higher voltages (2-3 V). Not even at higher voltages this dependence is not exponential to sustain a hopping mechanism. The most important conclusion is that it is possible the injection of intense currents through this structure.

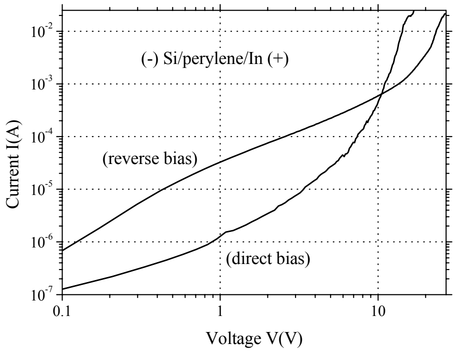

Fig. 3. I-V plot of silicon/perylene/In heterostructure.

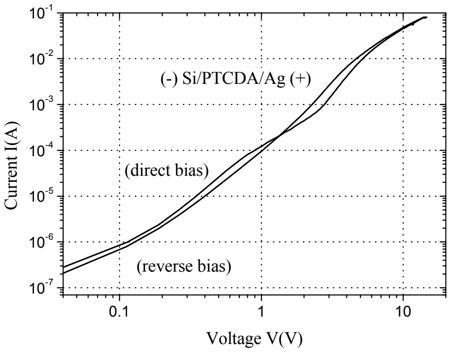

Fig. 4. I-V plot of silicon/PTCDA/Ag heterostructure.

The linear I-V dependence of perylene/Ag contact (Fig. 5) for voltages <0.7 V becomes at higher voltages a power dependence with n=2 suggesting the appearance of the SCLC phenomenon and then with n=3 associated with the presence of defects (traps) in the organic semiconductor band gap. At high currents this dependence is linear, but in time appears the degradation of the structure.

An ohmic behaviour is emphasised also for perylene/Ga contact for voltages ~ 1 V (Fig. 6). For higher voltages there is a continuous transition through power I-V dependence with n=4, dependence associated with SCLC and defects in the band gap (Fig. 6).

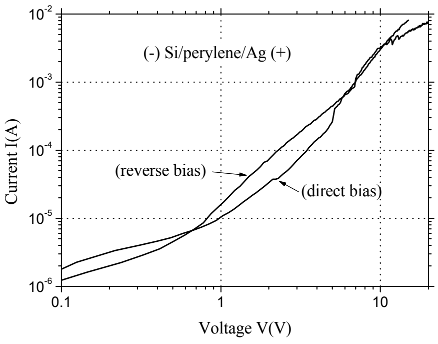

Fig. 5. I-V plot of silicon/perylene/Ag heterostructure.

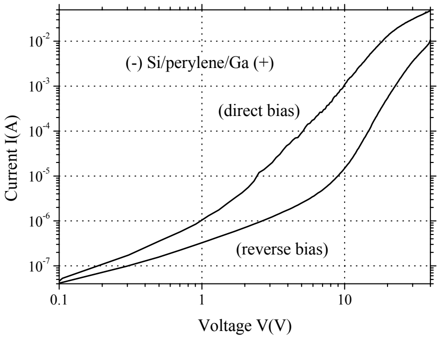

Fig. 6. I-V plot of silicon/perylene/Ga heterostructure.

A special behaviour is evidenced for PTCDA/Ga contact (Fig. 7): for voltages >2 V there is a difference of 2-3 orders of magnitude between the direct and reverse current. At high currents and reverse bias the exponent of the power dependence is n=2 for voltages <10 V and at direct bias for voltages >10 V, suggesting a space charge limited current conduction mechanism. For direct bias at voltage < 2 V the dependence is ohmic and for reverse bias there is no ohmic dependence.

The most important characteristic of In, Al, Ag and Ga diffusion process in organic layer is the high level of incorporation of isolated atoms and absence of clustering [42]. This high diffusivity can be attributed to a relatively low first ionisation energy that favours the transfer of an electron to the host organic matrix, ionisation leading to Coulomb type repulsion between positively charged In ions in interstitials sites (organic crystalline materials are characterized by large dimension interstitials zones), acting as driving force for diffusion. The diffusion rate is also substantial for the other selected metals but slowly decrease in the succession: In>Al>Ga because the first ionisation energy for these metals increases in the following succession: In (5.78 eV)<Al (5.98 eV)<Ga (6 eV). 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 to the clustering process. Metal with high value of the first ionisation energy, as Ag and Cu remain neutral at the surface of the organic film and form clusters.

A distinct type of structure is silicon/m-DNB/Cu (Fig. 8) characterised by a strong increase in the current for voltages between 0-10 V and a close linear behaviour for higher voltages between 10-20 V.

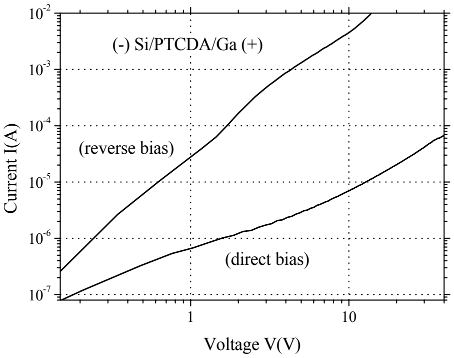

Fig. 7. I-V plot of silicon/PTCDA/Ga heterostructure.

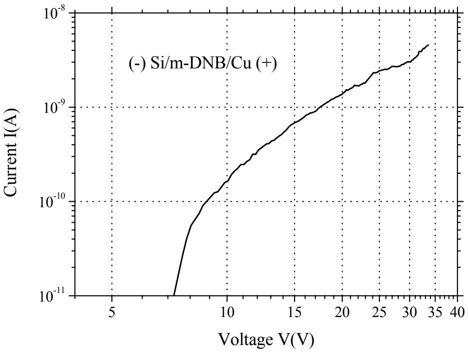

Fig. 8. I-V plot of silicon/m-DNB/Cu heterostructure.

Modification in the morphology of the film determined by the quality correlated with the preparation conditions especially for rapid thermal solidified films of m-DNB can determine a modification of the I-V characteristics from linear to power ones with an exponent n=2 associated with SCLC and defects in the band gap.

So there are two counteracting factors affecting the electrical behaviour of the organic/metal contact: the motion of the metallic atoms through the organic film determining the penetration deep correlated with Coulomb repulsion and the chemical reaction with the substituent group that limits the motion. The metal atoms diffusion stops when the saturation of the organic film takes place or the front of the molecules, which have not reacted, are too deep below the surface of the organic film.

4. Conclusions

The main contribution of this paper is in the field of the properties of In, Al, Ag, Ga, Cu contact with perylene, PTCDA and m-DNB.

Most of the investigated organic semiconductor/metal structures present ohmic behaviour only in the low voltages range that change at high voltages in power behaviour with an exponent n=2 PTCDA/Ag; perylene/Ag; PTCDA/Al; PTCDA/Ga) associated with space charge limited current phenomenon and n=3 (PTCDA/Ag, perylene/Ag, perylene/Ga) associated with the presence of defects in the organic semiconductor band gap. Exception is represented by perylene/Al contact with linear behaviour only at very low voltages (<0.03 V). Other particularities were evidenced for perylene/In contact with reverse bias showing an exponential behaviour at high voltages (>10 V) and m-DNB/Cu contact with an ohmic behaviour at high voltages 10-20 V.

A special behaviour has been emphasised for PTCDA/Ga, which presents ohmic behaviour only for positive voltages <2 V and a space charge limited current conduction mechanism for high currents. Perylene/Ga contact is ohmic at voltages ~ 1 V.

We have remarked that perylene/Al interface is not characterised by high rates of diffusion of Al in perylene film and a very weak the reaction of aluminium with perylene compared to PTCDA. As a consequence there is not a high density of states below the Fermi level to be involved in the conduction mechanism and perylene/Al contact is deviated from an ohmic behaviour.

All the contacts investigated in this study are favourable to a carriers' injection mechanism in well defined voltage conditions (low voltages) and the only structure showing a hopping transport mechanism is In/perylene.

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*Corresponding author: fstanculescu@rdslink.ro