Photoelectrical characterization of a new low molecular weight compound

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Abstract. Photoelectrical characterization of a newly synthesized low molecular weight compound was carried out. 1,8-naphtalimide (chemical formula C₃₂H₃₄N₄O₅S) was originally synthesized and analyzed by NMR spectroscopy. Thin films were deposited in vacuum on commercially pre-patterned ITO covered glass substrates and the samples were prepared in clean room environment. The films deposited were characterized by SEM. Photoelectrical characteristics of the samples prepared were estimated by dark current-voltage measurement, spectral dependence of the photoconductivity and measurement under exposure with light, produced by solar simulator. Finally electroluminescence measurements were performed. It was found that the samples exhibit diode behaviour. The low values characterizing photovoltaic parameters obtained could be connected with the relative higher series resistance (Rseries). The predominant influence of Rseries is assumed as the relative high photoluminescence, measured from solution should be related to a relatively strong charge carrier photogeneration. This result is supported by electroluminescent measurement. Another reason for the low values of the photovoltaic parameters measured could be the non-optimized film thickness leading to a non-optimal light absorption and increased charge carrier recombination. The assumption for the predominant influence of Rseries is supported by the electroluminescent measurements.

1. Introduction

Organic materials are potential candidates as active thin semiconductor films in the microelectronic devices due to their easy processing and low cost.

Owing to their potential applications in the organic electronics, the development of new organic semiconductor materials has been an ever hot issue in the past decades. Application of pure oligomers and polymers bearing strictly defined substituents and degree of polymerization is crucial for successful preparation of organic electronic devices. However, preparation of such organic materials usually requires expansive multistep synthetic procedures, leading to low overall yield of the final
products. The low solubility of many light emitting polymers in organic solvents can be an additional obstacle for their purification.

Because of their strong fluorescence and excellent photostability, 1,8-naphthalimide derivatives have been widely used in light emitting diodes, in most cases as part of oligomers and polymers [1, 2]. The strong photoluminescence measured also shows that under some conditions effective solar cells could be prepared. To the best of our knowledge, the synthesis and application of low-molecular 1,8-naphthalimides for an application in the organic electronics is comparatively less investigated [3, 4, 5].

Thin films of small molecular weight semiconductors are usually prepared by means of a variety of complex techniques including physical or chemical vapour deposition, organic molecular beam epitaxy or solution-based deposition techniques. The performance of small molecular weight organic devices has been shown to be highly sensitive to film morphology and processing conditions. Often, the solution deposited active layers of devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates whereas the vapour deposition techniques provide high quality crystalline films, characterized by improved charge transport properties compared with those of solution deposited films.

This work reports a photoelectrical characterization of vacuum deposited thin films from newly synthesized by simple procedures and cheap commercially available precursors – low-molecular 1,8-naphthalimide derivatives.

2. Experimental

1,8-naphthalimide (chemical formula C$_{32}$H$_{34}$N$_{4}$O$_{5}$S) hereafter denoted as MAX-06-02 (figure 1) was synthesized according to a procedure explained elsewhere. The synthesized material was purified by flash column chromatography. Elementary analysis was performed by NMR spectroscopy.

![Figure 1. Chemical structure of the active organic semiconductor material MAX-06-02 (C$_{32}$H$_{34}$N$_{4}$O$_{5}$S). Molecular Weight: 586.71. Elemental Analysis: C, 65.51; H, 5.84; N, 9.55; O, 13.63; S, 5.46.](image)

For fabrication of the samples “Ossila OLED/OPV Pixelated Anode Substrate System” and Ossila encapsulation system were used. It consists of pre-patterned ITO-covered glass substrate with standard active area of 0.06 cm$^2$, mask for the organic film deposition, cathode deposition mask, encapsulation epoxy, encapsulation glass slides and electrical connection legs with standard 0.1 inch (2.54 mm)
pitch. The pre-patterned ITO structure consists of one cathode strip by the long side of the substrate and six fingers which combined with deposition masks forms six active pixels with dimensions 4×1.5 mm and six anodes connected to them. The pre-patterned ITO structures were cleaned by sonication in 10% NaOH water solution, de-ionized water and isopropyl alcohol followed by nitrogen blowing for drying.

The subsequent active semiconductor and electrode films were prepared in the clean room class C, to prevent the dust and particles from disrupting the thin layer. The clean lab is equipped with MB-200B MBRAUN gloveboxes (M. Braun Inertigas-Systeme GmbH, Garching, Germany). Oxygen sensitive materials were stored and manipulated exclusively in the nitrogen gloveboxes, where also most of device fabrication step took place.

The MAX-06-02 thin film was deposited onto Ossila substrates in the vacuum system from thermally heated sources at evaporation temperatures of 180 °C and deposition rate of 2.5 Å/s through the active area deposition mask. The deposition rate was controlled by quartz crystal microbalance. After deposition of the active composite layer, the samples were taken out in nitrogen atmosphere, the mask was changed and vacuum deposition of aluminum was performed. The aluminum cathode of 150 nm film thickness was thermally evaporated in 1×10^{-6} mbar at a deposition rate of 1 Å/s.

Finally the structures were encapsulated by epoxide resin, which was hardened for 30 minutes under UV lamp irradiation. After that the samples were removed from the glovebox and provided with contacts for electrical measurements.

![Figure 2](image.jpg)

**Figure 2.** SEM image of the deposited MAX-06-02 thin films taken at a magnification of 20000.

Then the samples were checked by optical microscopy for film imperfections and a possible overlapping of the layers.

Selected samples were studied by Scanning Electron Microscope (SEM) Philips 515. The SEM morphology characterization of the MAX-06-02 films was carried out on the Ossila substrates without implementing the final encapsulation procedure.

The setup for measurement of dark $I-V$ characteristic and the spectral dependencies of the photocurrent consists of Keithley 6517A electrometer including a voltage source. Monochromatic light was produced by LOT-Oriel halogen lamp LSH502 and LOT-Oriel monochromator MSH101. Light power was measured by the S120VC - Standard Si Photodiode Power Sensor and Keithley 485 picoampermeter.

Dark $I-V$ characteristics were measured in both directions of the voltage scale. Spectral dependence of the photocurrent was measured at zero applied voltage in the range of 250÷550 nm then the
dependence of the photocurrent on the incidental light power (irradiance) was measured. For this measurement the sample was exposed to monochromatic light at a wavelength of 395 nm.

Selective photoconductive samples were measured under exposure of a standard light produced by solar simulator LS0916 LOT Oriel class AAA, which provides defined light source according to standard AM 1.5. Incident light intensity was about 1000 mWcm$^{-2}$ and was controlled by calibrated reference silicon cell RR200O from ReRa systems (ReRa Solutions BV; Nijmegen, Netherlands). For the studied samples, the exact irradiation of 953 mWcm$^{-2}$ was measured. In this case the current voltage measurements were executed by electrometer Keithley 2601B (Keithley Instruments Inc., Cleveland, OH, U.S.A.).

3. Results

3.1. Characterization

The film surface characterization of the MAX-06-02 films was performed by SEM. The SEM image presented in figure 2 is taken at a magnification of 20000 before applying the encapsulation procedure. The SEM image shows that smooth and uniform MAX-06-02 films without a presence of pinholes were obtained. The predominant part of the surface area is flat which facilitates the deposition of subsequent layers. In general it could be concluded that the smoothness and the uniformity of the films obtained is a good prerequisite for a formation of an interface without voids between the contacted electrode and semiconductor surfaces. As a consequence the ITO|MAX-06-02|Al samples prepared will be suitable for electrical measurements in a “sandwich” type electrode configuration.

3.2. Photoelectrical measurements

$I$-$V$ characteristics measured in dark on ITO|MAX-06-02|Al structures with active MAX-06-02 films of about 150 nm thickness are presented in figure 3. To estimate the electrical parameters of the samples, the graphs are plotted in a semilogarithmic scale (negative values of the current are multiplied by -1).

![Figure 3](image1.png)

**Figure 3.** $I$-$V$ characteristics measured in the dark.

![Figure 4](image2.png)

**Figure 4.** Spectral dependence of the photocurrent at zero applied voltage.

From the dark current measurements, non-linear and unsymmetrical characteristics are obtained. Comparing the curves measured in forward and backward direction on the voltage scale a rectification ratio of more than 3 orders of magnitude was found. This clearly shows that the conductivity is predominantly contact limited and the sample behaves as a diode. It should be mentioned that no
additional intermediate layers serving to reduce the contact barrier were used. The optimization of the stacked multilayer structures could be a subject of a future study.

Spectral dependences of the photocurrent, measured at zero applied voltage between the electrodes from ITO|MAX-06-02|Al structures with active MAX-06-02 films are presented in figure 4. The spectrum consists of a wide single peak centered at 395 nM. The wide peak shows that a relative broad sensitivity in an extended spectral region could achieve. For this purpose the representative samples were exposed to a white standard light. The data obtained from the solar simulator are summarized in table 1. The measurements show low values of \( I_{SC} \) and \( V_{MP} \), and consequently \( V_{PP} \), and \( \eta \). This result could be related to the relative high value of the series resistance. This effect is more probable as other experiments show a relative high photoluminescence measured from solution.

| parameter | dimension | value       |
|-----------|-----------|-------------|
| Size      | [cm\(^2\)] | 0.06        |
| Irradiance| [W/m\(^2\)] | 952.9       |
| \( I_{SC} \)  | [mA]    | \( 2.67 \times 10^{-6} \) |
| \( V_{OC} \) | [mV]   | 542         |
| \( I_{MP} \) | [mA]   | \( 1.86 \times 10^{-6} \) |
| \( V_{MP} \) | [mV]  | 318         |
| \( P_{MP} \) | [mW] | \( 5.93 \times 10^{-7} \) |

The electroluminescence (figure 5) measurements could add more information about the photoelectrical properties of the samples prepared. The \( I-V \) characteristic measured in an extended area of voltages applied on the samples confirms the diode behaviour of the samples. The first part at the \( I-V \) characteristic measured at low voltages is clearly related to a slope less than 1, which is typically connected with a contact limited current. The absence of space charge limited and double injection areas at higher voltages (\( I \sim U^{-2} \)) also supports this state. In general the slope of the \( I-V \) characteristics is gradually changed from less than 1 to 8 instead.

**Figure 5.** Electroluminescence measurements of the samples prepared.
4. Conclusion
Photoelectrical characterization of a newly synthesized low molecular weight compound was carried out. The samples exhibit clear diode-like behavior. The low values for a characterizing photovoltaic parameters obtained could be connected with the relative higher series resistance. The predominant influence of $R_{\text{series}}$ is assumed as the relative high photoluminescence, measured from solution should be related to a relatively strong charge carrier photogeneration. This result is supported by electroluminescent measurement. Another reason for the low values of the photovoltaic parameters measured could be the non-optimized film thickness leading to a non-optimal light absorption and increased charge carrier recombination. The assumption for the predominant influence of $R_{\text{series}}$ is supported by the electroluminescent measurements.

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