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Molecular Semiconductors — Doped Insulator (MSDI) Heterojunctions as New Conductometric Devices for Chemosensing in Wet Atmosphere

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Abstract: Most gas sensors are based on inorganic materials. These are either resistors, diodes or transistors. A few conductometric sensors have been designed around molecular materials. In 2009, new sensors, called MSDI devices, were built around a heterojunction between a molecular semiconductor (MS) and a doped-insulator (DI). In those sensors, the MS layer must be more conductive than the DI sublayer to take advantage of the heterojunction by forcing the current through its interface. In MSDI sensors, the MS is generally a p-type material and DI can be either a p-type (p-MSDI) or n-type (n-MSDI) material. The energy barrier across the interface depends on the difference in the charge carrier density within the two layers. In this study, we used this new transducer to detect different gases. We studied, in particular, the response of MSDIs to ammonia in a broad range of relative humidity (rh). A n-MSDI exhibits a positive response to ammonia (electron donating species) and a negative response to ozone (oxidizing species). These responses are opposite to those of a resistor prepared using only this material ($LuPc_2$), despite the p-type MS layer ($LuPc_2$) being the only material in contact with the gas. The better stability toward humidity was obtained with $Cu(F_{16}Pc)$ as n-type sublayer. Thus, for $Cu(F_{16}Pc)/LuPc_2$ MSDI (50 nm/50 nm), the relative response to NH_3 is almost not affected by the variation of rh in the 20-80 % range.

Keywords: Conductometric transducer; gas sensor; ammonia; humidity; MSDI; heterojunction

1. Introduction

The need for information on air quality inside buildings and outdoors, as well as the industrial need for *in situ* analytical tools capable of monitoring processes without the externalization of samples in laboratories, has led to a steep increase of the demand for gas sensors capable of operating in real-world conditions. Such sensors must perform quite well since they are exposed to atmospheres subject to wide humidity variations. This is particularly true for ammonia sensors (NH_3) since both NH_3 and H_2O molecules are capable of interacting with the sensing material through hydrogen bonding and dipole-dipole interactions. As a result, NH_3 and H_2O molecules exhibit similar affinities towards sensing materials and affect them in similar ways. However, when using conductometric transducers it is possible to take advantage of the stronger electro-donating character of NH_3 compared to that of H_2O in order to achieve some measure of selectivity.

One way to get rid of the interference of water in NH_3 sensing is to use sensors based on Molecular Semiconductor − Doped Insulator heterojunction (MSDI) [1]. These sensors are composed of two stacked layers of molecular materials. While the top layer only is exposed to the gas, the nature of the sensing response is determined by the bottom layer (Fig 1). All MSDIs with a p-type sublayer exhibit a negative response to NH_3, similar to that of $LuPc_2$ resistors, whose majority charge carriers are positive in air. However, n-type MSDI exhibit an opposite response despite the fact that the only material exposed to NH_3 is the $LuPc_2$ upper layer for both kind of MDSI heterojunctions. This can be explained as resulting from the decrease of the energy barrier at the MS-DI interface [1,2,3].

The unique properties of the lutetium *bis*phthalocyanine ($LuPc_2$) result from its radical nature that makes it highly sensitive to redox active species [4].
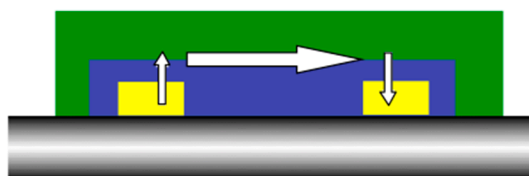

Figure 1. Schematic side view of an MSDI heterojunction. The arrows indicate the main charges flow from one electrode to the other.

The present work aims at discussing the effects of the sublayer thickness on the response of sensors based on a MSDI architecture. All reported MSDI are made using $LuPc_2$ as upper layer and one perylene derivative as n-type sublayer: either the perylene tetracarboxylic dianhydride (PTCDA) or the *bis*heptafluorobutyl perylene tetracarboxylic diimide (C_4F_7-PTCDI). The performance of both sensors will be compared with those of MSDIs made with $Cu(F_{16}Pc)$ as sublayer.

2. Experimental Section

All measurements were performed at room temperature, using a Keithley 6517A electrometer equipped with an embedded DC voltage supply. Gas sensing experiments were performed using 1 min/4 min exposure/recovery cycles, at a flow rate of *ca.* 0.5 nccm. For experimental details see [5] (Fig. 2).
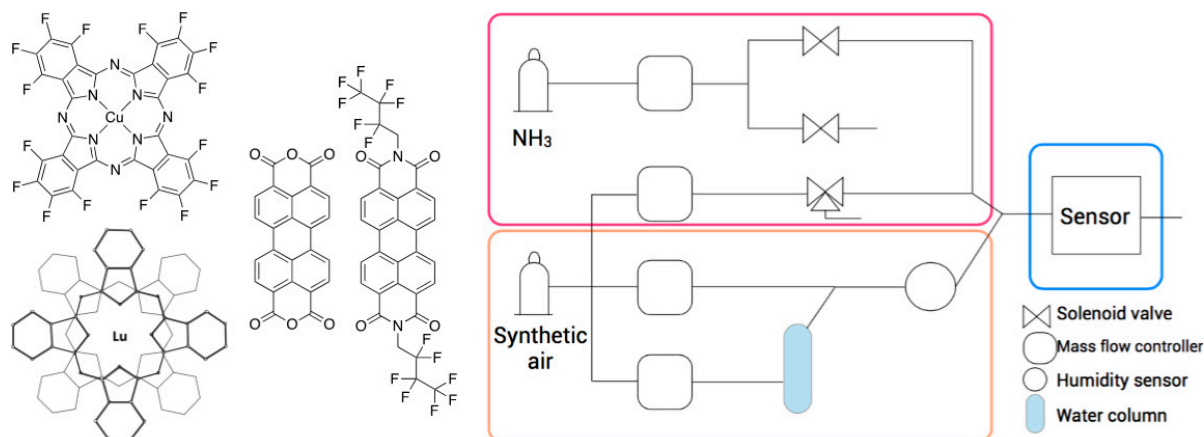
Figure 2. Schematic molecular structures of Cu(F$_{16}$Pc), (top left), PTCDA (middle), C$_4$F$_7$-PTCDI (right) and LuPc$_2$ (bottom left), and scheme of the ammonia workbench.

2.1. Samples

All samples will be identified based on the nature and the thickness of their sublayer and of their top layer. For instance, the MSDI PTCDA/LuPc$_2$ 30/70 sensor is made of 70 nm of LuPc$_2$ as top layer deposited on a 30 nm thick PTCDA bottom layer (Fig. 2).

3. Results and Discussion

The energy levels of the molecular materials studied in this paper were determined by ultraviolet photoelectron spectroscopy (UPS) and inverse emission photoelectron spectroscopy (IEPS), for PTCDA and LuPc$_2$ and from cyclic voltammetry and optical energy gap for C$_4$F$_7$-PTCDI (Fig. 3) [6].
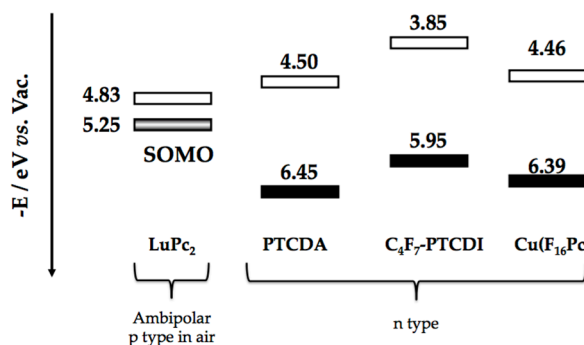

Figure 3. Schematic view of the energy levels LUMO (white) and HOMO (black) or SOMO (grey) involved in the electrical properties of PTCDA and PTCDI derivative, obtained from photoelectron spectroscopies (UPS and IEPS) for LuPc$_2$ [6] and PTCDA, and from cyclic voltammetry and optical energy gap for C$_4$F$_7$-PTCDI.

The energy of the LUMO in C$_4$F$_7$-PTCDI, which is quite high compared to other air-stable n-channel semiconductors, was obtained from its reduction potential and the energy of the HOMO was deduced from its optical energy gap and its LUMO position. PTCDA and C$_4$F$_7$-PTCDI can easily transport electrons, whereas LuPc$_2$ can easily give and accept electrons. As depicted in Fig. 3, the energy gap is small for LuPc$_2$ (*ca.* 0.4 eV) and larger for perylene derivatives (*ca.* 2.0 eV). These energy gap values explain the high conductivity of LuPc$_2$ and the poor conductivity of perylene derivatives [7].

3.1. Protocol

For a better comparison of the results and to improve repeatability, on principle, experiments on the sensors were all conducted following the same sequence. First, the current-voltage characteristics (I(U)) of each MSDI device have been measured between -5 V and +5 V, at a sweep rate of 0.1 V.s^{-1}, taking one point every second. Then NH$_3$/humidity experiments were carried out, during which the sensor was exposed to several concentrations of NH$_3$ under humid air atmosphere.

3.2. I(U) characteristics

The I(U) characteristics of MSDI heterojunctions are specific to this kind of device (Fig. 4). The MSDIs exhibit non-linear I(U) behavior contrarily to common resistors made of a single layer of molecular material, which follow Ohm's law.
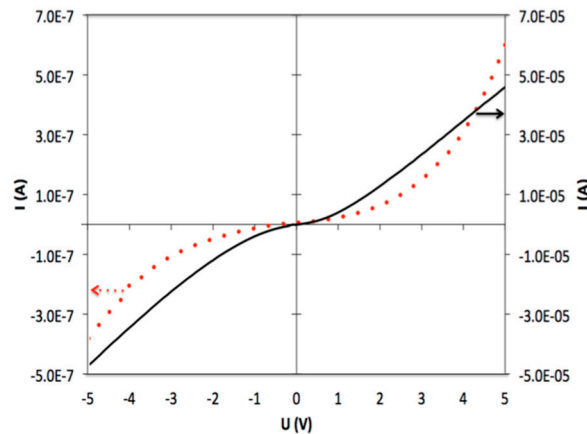

Figure 4. I(U) characteristics of a PTCDA/LuPc$_2$ 30/70 sample (solid line) and a C$_4$F$_7$-PTCDI/LuPc$_2$ 50/50 film (dotted line), from -5 V to $+5$ V.

This is the result of the existence of an energy barrier between the MS and the DI layers. The charge carriers always go through the most conductive pathway by travelling across the quite insulating DI layer to the much more conductive MS layer (the interelectrode distance is about three orders of magnitude longer than the thickness of the DI sublayer). This means that the mobile charges do cross the interface between the two layers twice. The observed energy barrier can be explained by the opposite sign of the majority charge carriers in each material (positive in LuPc$_2$ and negative in perylene derivatives). This effect is stronger when using the PTCDI derivative than with the PTCDA sublayer and can be explained by the presence of the fluorinated chains that make the charge transfer with the LuPc$_2$ upper layer even more difficult. This is also the reason why a lower current, by a factor of 100, is observed (Fig. 6). The LuPc$_2$ resistor shows a decrease of the measured current during ammonia exposure, as expected for a p-type semiconductor exposed to an electron donating gas [8], whereas the perylene/LuPc$_2$ MSDI heterojunctions show a current increase in the same conditions. In both cases the only material in contact with the atmosphere is LuPc$_2$. MSDI heterojunctions have been described in more details in a previous work [1].

3.3. Gas sensing

To determine the effect of water on the NH_3 sensing properties of the devices (relative response), concentration of NH_3 was varied under each tested relative humidity (rh) level. The optimized sample (PTCDA/LuPc$_2$ 50/50) was exposed to NH_3 from 30 to 10 ppm under synthetic air loaded with 70 to 10 % rh (Fig. 5). On this sensor, NH_3 induces an increase in intensity of the measured electrical current. The higher the concentration, the greater is the increase. After exposition, the measured current returns to the baseline. The sensor response is fully reversible.
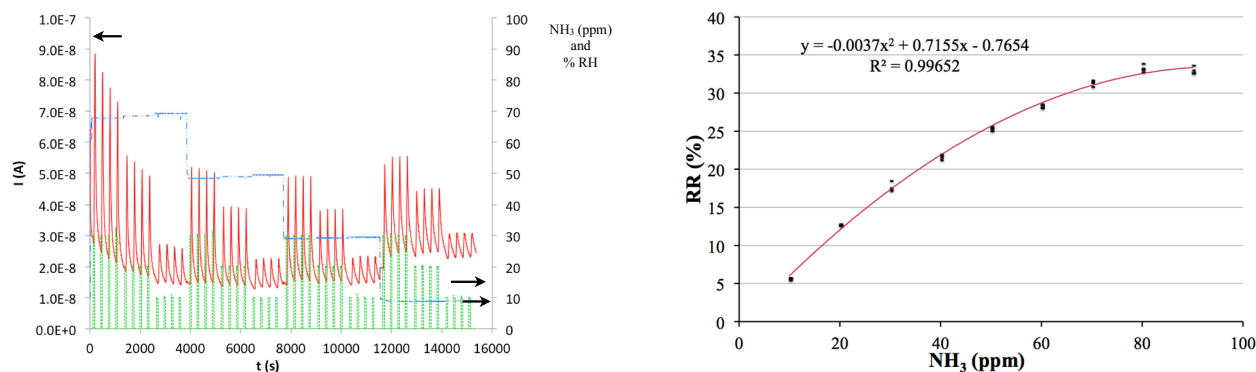

Figure 5. (left) Current as a function of time for a PTCDA/LuPc$_2$ 50/50 MSDI device submitted to 1 min/4 min NH_3/rh exposure/recovery cycles, when polarized at 0.3 V. **(right)** Relative response ($\Delta I/I_0$) of a C$_4$F$_7$- PTCDI/LuPc$_2$ 50/50 MSDI as a function of the NH_3 concentration at 50 % rh, computed from the mean value of four exposure/recovery cycles.

The effect of water on the current baseline appears to be quite small, except at low rh. Relative responses (RR) were calculated for each cycle under each rh level and plotted as a function of the rh. Such kind graph highlights the effect of water on NH_3 sensing while showing the discrimination between various NH_3 concentrations. Increasing NH_3 concentrations by 10 ppm results in an important increase of the RR. This RR ranges from 28 to 70 % at 10 ppm NH_3 when rh varies from 10 to 70 %. The RR ranges from 87 to 169 % under 20 ppm of NH_3 and from 183 to 252 % under 30 ppm NH_3. There is no overlap between the RR measured at 10, 20 and 30 ppm, independently of the rh in the range 10-70 %. Also, these are quite high figures compared to most NH_3 sensors. For C$_4$F$_7$-PTCDI/LuPc$_2$ 50/50 film, we observed a small sensitivity rh variation of the response to NH_3. A shift of the baseline of less than 10% was measured between 10 and 70 % rh. In order to determine the sensitivity to NH_3, measurements were performed by steps of 10 ppm, from 10 to 100 ppm, at 50 % rh (Fig. 5 right).

4. Conclusions/Outlook

PTCDA/LuPc$_2$ MSDIs exhibit a high sensitivity to ammonia with a good reversibility. The thickness effect can be the result of a modification of the weight of the interface in the device, but also of a modification of the morphology of layers. Cristallinity and roughness of layers of molecular materials are known to be dependant on their thickness [9]. A good discrimination between the studied ammonia concentrations (better than 10 ppm) was observed in a broad range of rh.

Conflicts of Interest

The authors declare no conflict of interest.

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