

# Interaction of Metals with Perylene Derivatives as a Model System for Contact Formation in OFET Structures

Beynor. A. Paez\*, Georgeta Salvan, Reinhard Scholz,  
Thorsten U. Kampen and Dietrich R. T. Zahn

*Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany*

## ABSTRACT

The understanding of metal/organic interfaces is fundamental for achieving high quality contacts in organic based field effect transistors, OFETs. Here the formation of In and Ag interfaces on 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and N, N' dimethyl-3,4,9,10-perylene tetracarboximide (DiMe-PTCDI) is investigated by *in situ* Raman spectroscopy. Upon metal deposition a significant enhancement of the Raman signals arising from internal vibrational modes is observed for these two perylene derivatives, clearly indicating the presence of surface enhanced Raman scattering (SERS). Molecules in direct contact with the metal are involved in a weak dynamical charge transfer in the electronic ground state, resulting in a breakdown of the Raman selection rules for the free molecule. Both metals show very weak interactions with the organic thin films. This finding is opposite to previous suggestions of covalent bond formation between In and O atoms in PTCDA. The Raman scattering of molecules close to the metal interface is enhanced by coupling to the plasmon resonance of small metal clusters, indicating a high roughness of the metallic film. The enhancement factors can be used to extract information on diffusion of the metal atoms into the organic film and on the morphology of the contact layer.

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## 1. INTRODUCTION

Organic molecules are at the basis of many novel devices such as organic light emitting diodes (OLEDs)<sup>1</sup> or organic field effect transistors (OFETs), both promising candidates for applications with flexible or transparent plastic substrates.<sup>2,3</sup> For the active layer in these devices, different organic compounds have been investigated in great detail, including polyacenes, thiophenes, perylene derivatives, phthalocyanines, and Alq<sub>3</sub>.

The optical properties of different perylene derivatives have been addressed by several experimental and theoretical studies, covering single molecules, poly-crystalline thin films and single crystals.<sup>4</sup> The optical band gap in the visible and other microscopic properties like the rather large mobilities of the charge carriers are suitable for opto-electronics applications.<sup>5</sup> Depending on the substrate, highly ordered crystalline films can be grown, resulting in favourable conditions for charge transport.<sup>6-8</sup> In particular, the stacking of the molecules produces a rather large overlap between the  $\pi$  orbitals of neighbouring sites, resulting in an anisotropy of the mobility tensor.<sup>9</sup> The perylene derivatives N,N'-dimethyl-3,4,9,10-perylene tetracarboxylic diimide (DiMe-PTCDI) and 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) are considered to be good candidates for organic electronic devices due to the possibility to create ohmic or rectifying contacts with different metals.<sup>10,11</sup>

As the device performance is strongly influenced by these contacts,<sup>12</sup> the present study is devoted to the formation of the interface between a thin film consisting of PTCDA or DiMe-PTCDI and different metal contacts deposited on the organic layer. It will be shown in detail that Raman spectroscopy is a suitable technique for the analysis of the reactivity between the metal atoms and the organic molecules.

\*corresponding author, b.paez@physik.tu-chemnitz.de

## 2. EXPERIMENTAL

The organic molecular beam deposition (OMBD) was performed in an ultra high vacuum (UHV) chamber aligned with a Raman spectrometer, cp. Fig. 1.<sup>4,13</sup> The perylene derivatives PTCDA and DiMe-PTCDI obtained from Syntec GmbH Wolfen were pre-purified by two sublimation steps prior to the deposition of the organic layers. The organic materials and the metals were evaporated from Knudsen cells kept at 280° C for PTCDA, 270° C for DiMe-PTCDI, 830° C for In, and 930° C for Ag, resulting in deposition rates of 0.3 nm/min for both perylene derivatives, 1 nm/min for In and 1.6 nm/min for Ag, respectively. As described elsewhere in more detail, the substrates used were sulfur-treated GaAs (100) annealed at 420° C prior to the deposition of the organic films.<sup>4</sup> During the growth of these films, the substrates were held at room temperature.

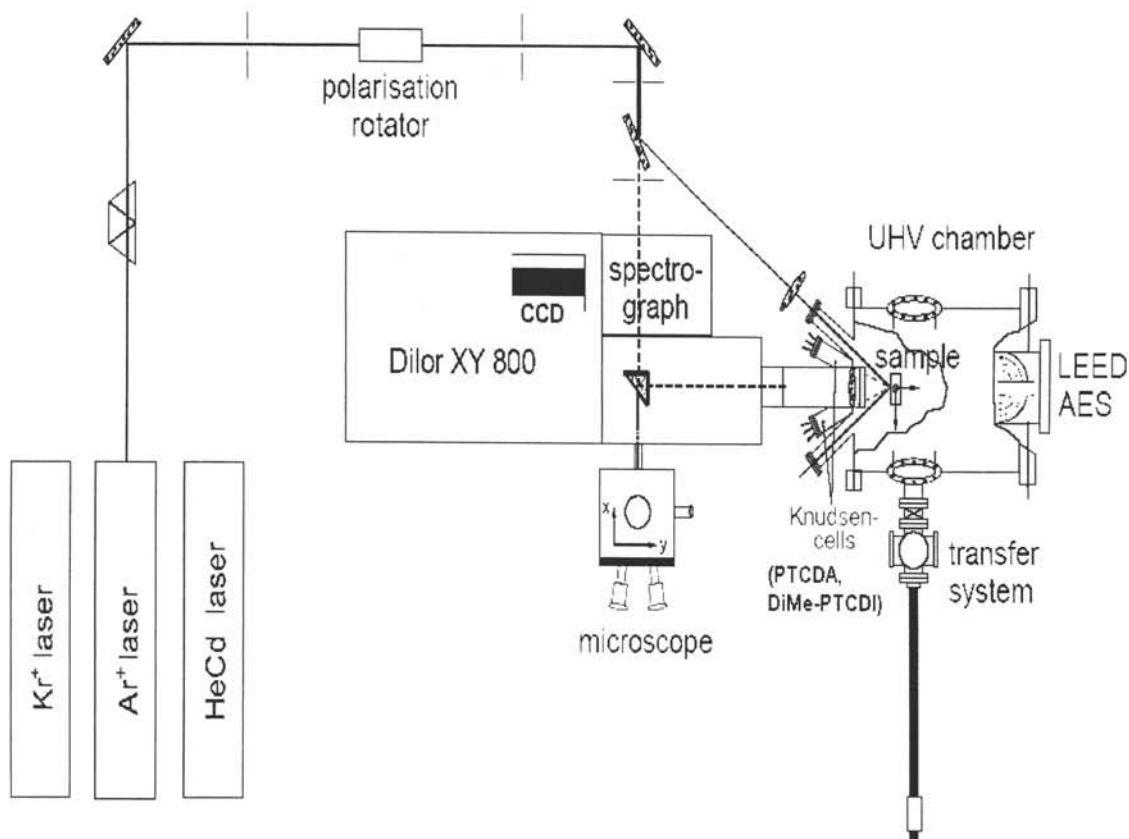
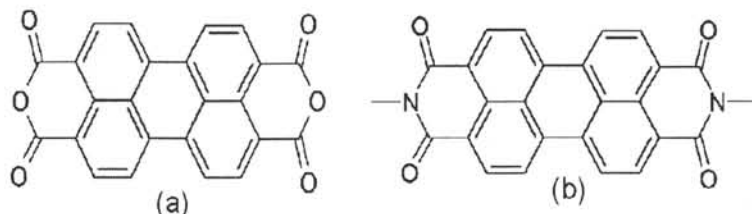


Figure 1. Experimental set-up.

The UHV chamber is optically aligned to a triple monochromator Raman spectrometer (DILOR XY) consisting of a equipped with a CCD camera for multichannel detection, allowing *in situ* Raman measurements during the film deposition. The Raman spectra were obtained by exciting the samples with an Ar<sup>+</sup> laser using the 488 nm (2.54 eV) line.

### 3. ORGANIC COMPOUNDS AND FILM MORPHOLOGY

In Fig. 2 the structural formulas of PTCDA and DiMe-PTCDI are depicted. PTCDA consists of 24 carbon atoms, 8 hydrogen atoms and 6 oxygen atoms, with a perylene core and four carboxylic and two anhydride groups bonded to each side of the perylene core. Due to its planar rectangular structure, the PTCDA molecule belongs to the  $D_{2h}$  point group.



**Figure 2.** Structural formula of the organic molecules: (a) 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and (b) N, N'-dimethyl-3,4,9,10-perylene tetracarboxylic diimide (DiMe-PTCDI). The hydrogen atoms of the perylene core and of the methyl groups are omitted.

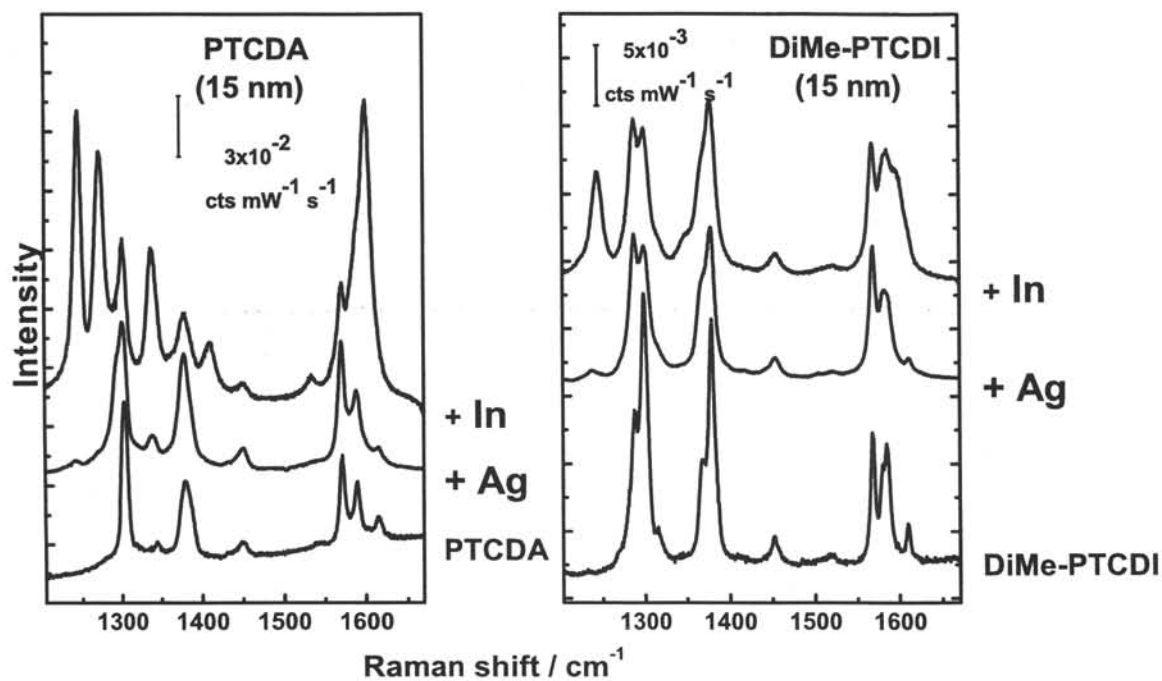
DiMe-PTCDI is similar to PTCDA but each of the two oxygen atoms in the anhydride groups is replaced by a nitrogen atom with its third bond terminated by a methyl group ( $N - CH_3$ ). Owing to the larger size of these imide groups with respect to an oxygen atom, DiMe-PTCDI exhibits a different geometric shape and as a consequence a slightly different electronic structure. The deviations from planarity result in a smaller point group depending on the orientation of the terminal methyl groups. Both for PTCDA and DiMe-PTCDI, the frontier orbitals are mainly localized on the perylene core, resulting in similar optical and electronic properties. However, the film morphology is strongly influenced by the methyl groups: Contrary to the flat-lying PTCDA molecules,<sup>14</sup> the stacking direction of DiMe-PTCDI molecules are tilted with a specific direction of the GaAs substrate plane.<sup>8, 15</sup>

### 4. INTERACTION BETWEEN PERYLENE DERIVATIVES AND METAL CONTACTS

After depositing the contact metals with a nominal thickness of 8 nm on the underlying 15 nm thick organic films, the Raman signals displayed in Fig. 3 are strongly enhanced. This phenomenon known as Surface-Enhanced Raman Scattering (SERS) is related to a coupling between the electronic transition in the molecules and the plasmon resonance in metal clusters with a diameter of a few nm. Among the two enhancement mechanisms involved in SERS, a dynamical charge transfer favours the molecules in direct contact with the metal, whereas the enhancement of the local electric fields penetrates a few nm into the organic layers.<sup>16, 17</sup>

In contrast to the selection rule for the pure organic layer where the resonant Raman spectra are dominated by internal breathing modes of the molecules,<sup>18, 19</sup> the SERS mechanism enhances the cross sections of internal modes of different representations. Therefore, the prominent new features including e.g. the strong signal around  $1250 \text{ cm}^{-1}$  for In-covered organic films could reveal a molecular vibration with a representation differing from  $A_g$  or, alternatively, a chemical reaction between the organic molecules and the metal atoms, giving a different vibrational fingerprint of the new compound.

This question can be answered by looking at the Raman signals in the energetic region of the lowest internal breathing mode occurring at  $233 \text{ cm}^{-1}$  for PTCDA and at  $221 \text{ cm}^{-1}$  for DiMe-PTCDI, cp. Fig. 4. In both cases, a chemical reaction between a metal atom and an oxygen atom of the organic molecule would result in an increased mass of the new compound. As a consequence, the position of this mode would be modified by a large splitting, but the Raman spectra give no evidence for vibrational modes of any metal-organic complex.



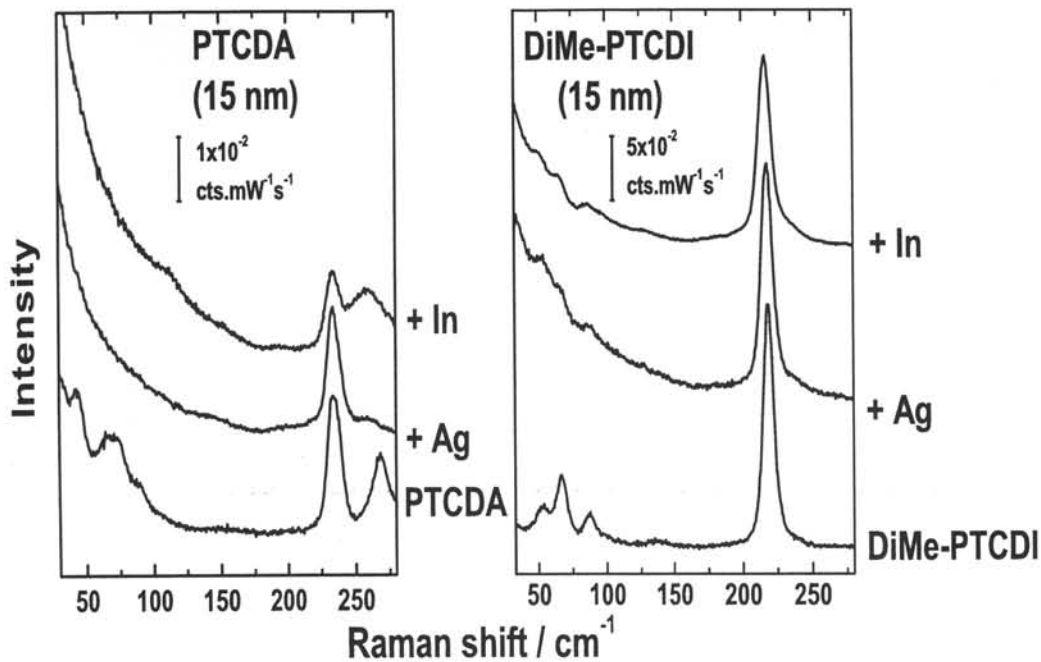
**Figure 3.** Raman spectra of 15 nm thick PTCDA and DiMe-PTCDI layers deposited on S-passivated GaAs substrates obtained at a laser wavelength of 488 nm (2.54 eV). The vibrational signature of the molecules is strongly modified by a subsequent deposition of indium or silver with a nominal thickness of 8 nm. The spectra obtained after the metal coverage are reduced by a factor of 0.017 for PTCDA and by 0.125 for DiMe-PTCDI.

Therefore, it can be concluded that both Ag and In do not react with the molecules, a finding corroborated by infrared spectra of similar films.<sup>15</sup>

From a comparison of the thick organic films displayed in Fig. 3 and Raman spectra obtained on a monolayer of the organic molecules covered with In or Ag it can be shown that all new features appearing in Fig. 3 are already present for a single organic layer. Moreover, the vibrational modes enhanced after Ag or In coverage occur in similar positions, including especially a similar size of the feature near 1250  $\text{cm}^{-1}$ . Therefore, the different Raman cross sections of this structure in Fig. 3 can be related to the different diffusion of In and Ag: The silver atoms remain at the surface of the organic film, in contrast to In diffusing deep into the organic layers. As a consequence, in the case of In coverage, the metal-organic interface is much larger than the film area, resulting in an enhancement of the Raman signals resulting from a larger fraction of the organic molecules in the film.

Since flat metallic layers present a penetration depth lower than 30 nm in the visible range, their surfaces should behave like mirrors for the electromagnetic waves, screening any interaction between the electromagnetic field and the metal surface. As a result the Raman signal of an organic layer covered by a flat metal layer should be dramatically attenuated with increasing metal layer thickness. The absence of this expected decrease of the Raman signals indicates a high roughness of the metal-organic interface, resulting in a predominance of the SERS effect over attenuation effects. As the silver atoms do not diffuse deep into the organic film, this roughness of the interface is directly determined by the surface morphology of the organic film.

In order to quantify the enhancement of the Raman signal after metal deposition, the area of different vibra-

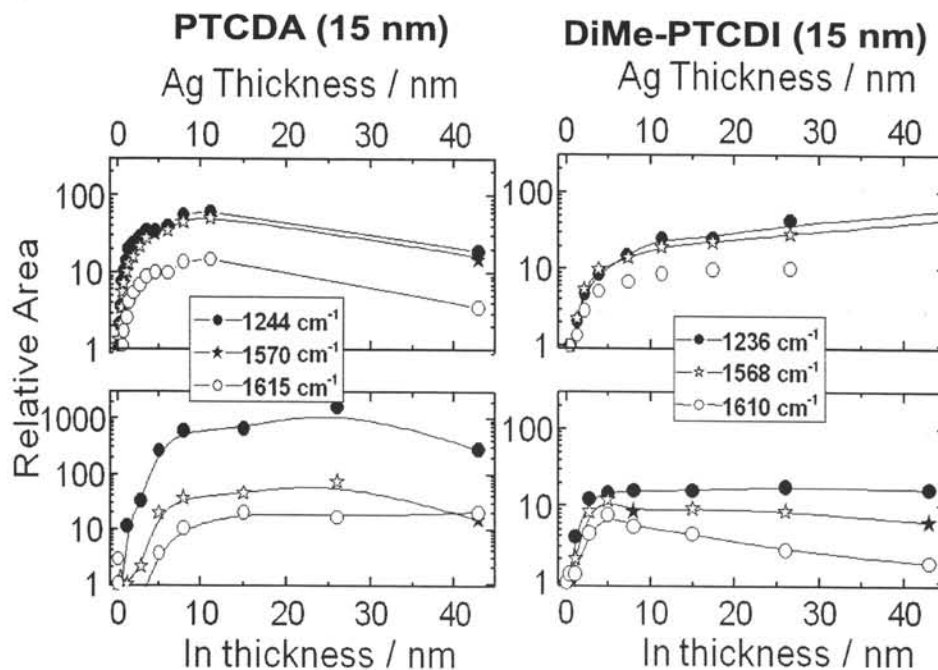


**Figure 4.** Raman spectra of the low frequency region of 15 nm thick PTCDA and DiMe-PTCDI films, before and after coverage with Ag or In.

tional peaks before and after metal deposition can be compared. Fig. 5 presents the corresponding enhancement factors, defined as the ratio of the peak area after metal deposition to the area of the corresponding structure in the Raman spectra of the uncovered organic film. Due to the larger area in the case of indium-organic interface, some modes are strongly enhanced, including especially an IR-active vibration of PTCDA at  $1244\text{ cm}^{-1}$  and a prominent mode at  $1602\text{ cm}^{-1}$ , cp. Fig. 3. However, for most other modes of PTCDA and DiMe-PTCDI, the more favourable resonance condition involving the plasmon of the silver clusters results in larger enhancement factors with respect to indium.

For silver covered PTCDA, the largest enhancement occurs for a nominal contact thickness of 10 nm, cp. Fig. 5, and for thicker metal layers the expected attenuation of the electromagnetic wave results in a decrease of the Raman signals. In the other three cases, the metal grows in a granular morphology, and the contact layer is not closed up to a rather large nominal thickness. Therefore, parts of the organic film can still contribute to the Raman signal for large nominal metal thicknesses before eventually the attenuation sets in.

When comparing PTCDA and DiMe-PTCDI, the PTCDA films show higher enhancement factors. For coverage with Ag, this fact is somewhat surprising because the absorption edge of DiMe-PTCDI is closer to the plasmon resonance in the metal clusters. Therefore, the small change in the chemical structure seems to be decisive: An efficient enhancement of the Raman signals via the SERS effect could possibly be reduced by the larger size of the methyl-imide groups, resulting in a larger distance between the aromatic core of the molecule and the metal clusters.



**Figure 5.** Enhancement factors of selected vibrational modes of PTCDA and DiMe-PTCDI after silver and indium coverage.

## 5. SUMMARY

In this work the formation of In and Ag interfaces with 3,4,9,10 - perylene-tetracarboxylic dianhydride (PTCDA) and N, N dimethyl - 3,4,9,10- perylene - tetracarboximide (DiMe-PTCDI) were investigated by in situ resonant Raman spectroscopy, in order to determine the interaction between the metals and the organic molecules. Using PTCDA and DiMe-PTCDI films contacted with In or Ag, the vibrational spectra reveal no evidence for chemical reactions between the metal atoms and the organic compounds. Contrary to silver, indium diffuses deep into the organic layer, increasing the area of the metal-organic interface and therefore the contact area. A significant enhancement of internal vibrational modes is observed in all cases, clearly indicating the presence of surface enhanced Raman scattering. The molecules having direct contact with the metal are involved in a weak ground state dynamical charge transfer, resulting in a breakdown of selection rules. The enhancement factors of the Raman signals can be employed to extract information on interdiffusion and morphology of the metal film.

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