Interaction between metals and organic semiconductors studied by Raman spectroscopy

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(Received 3 November 2003; accepted 29 March 2004; published 20 July 2004)

Silver and indium were deposited onto molecular layers of two perylene derivatives, viz. 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,N′-dimethylpyrpylene 3,4,9,10-dicarboximide (DiMe–PTCDI). The interaction between the metals and the organic semiconductors was probed in situ by Raman spectroscopy. The molecular structure is found to be preserved when Ag or In are deposited onto PTCDA and DiMe–PTCDI layers. For In, this is in contrast to previous suggestions of strong reactivity with PTCDA and covalent bond formation between In and O atoms in PTCDA. However, the molecules having direct contact with the metal are involved in a ground state dynamical charge transfer with different strength for Ag and In, resulting in a breakdown of vibrational selection rules. A significant enhancement of Raman internal vibrational modes is observed both for Ag and In deposition as a result of metal-induced surface enhanced Raman scattering (SERS). The enhancement factors observed for the internal modes reflect a rough morphology of the metal films which is influenced by the morphology of the underlying organic film. Moreover, conclusions regarding the indiffusion of the two metals can be drawn from the comparison of the breakdown of the selection rules for the internal modes and the spectral evolution of the external molecular modes. © 2004 American Vacuum Society. [DOI: 10.1116/1.1752897]

I. INTRODUCTION

The perylene derivatives 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and N,N′-dimethylpyrpylene 3,4,9,10-dicarboximide (DiMe–PTCDI) are considered to be good candidates for organic electronic devices due to the possibility to create ohmic or rectifying contact with different metals.1,2

Only few investigations of metal-on-organic interfaces are reported to date and those are mainly performed by means of electron spectroscopies. In particular, photoemission spectroscopy (PES) studies revealed that the Ag deposition onto PTCDA leads to the formation of an abrupt, nonreactive interface.2 Even though a thorough understanding of the vibrational properties of PTCDA molecules has been achieved from a combination of theoretical calculations and Raman spectroscopy measurements on crystals,3–5 most of the work devoted to metal/PTCDA interfaces, however, refers to the vibrational properties of molecular thin films deposited on either low index single crystal or rough metal substrates. Representative for the case of single crystal metal substrates are the studies of PTCDA on Ag(111) and Ag(110) by means of high resolution electron energy loss spectroscopy (HREELS) and electron energy loss spectroscopy (EELS).6,7

In the latter study new low-energy bands were observed and assigned to metal-induced states in the PTCDA HOMO–LUMO gap, apparently contradicting PES results. The rough substrates were found to induce surface enhanced Raman scattering (SERS).8 Recently a study was devoted to the in situ characterization of Ag deposition onto 15 nm thick PTCDA films grown on S-passivated GaAs(100) substrates.9 Regarding the In interface formation with the perylene derivatives there still is a discrepancy in the literature: PES studies indicate a strong reaction between In and PTCDA via the C=O bonds10 whereas more recent near edge x-ray absorption fine structure revealed the presence of a fractional charge transfer between the PTCDA or DiMe–PTCDI molecules and In.11

In this work Raman spectroscopy was employed for the in situ investigation of the interface formation between the metals and organic films with emphasis on the nature of interaction. The interface structure as well as the morphology of the metal films.

II. EXPERIMENT

Si-doped (N_d = 1.7–2.7×10^{19} cm^{-3}) GaAs(100) wafers provided by Freiberger Compound Materials were used as substrates. The cleaning and the S passivation of GaAs surface consisting of a wet chemical treatment followed by annealing under UHV was described in detail elsewhere.9 The organic molecules purchased from Lancaster Synthesis and Syntec GmbH and prepurified by two sublimation steps were thermally evaporated in ultrahigh vacuum (UHV) (base pressure ∼2×10^{-10} mbar) onto freshly prepared 2×1 reconstructed S–GaAs(100) substrates. The evaporation rate was 0.3 nm/min as determined by a quartz microbalance calibrated by means of atomic force microscopy. Two thicknesses of the organic interlayer were investigated: 15 nm and ∼0.4 nm, the latter being of the order of one monolayer (ML). The evaporation rates of Ag and In were 1.6 and 1 nm/min, respectively. In order to record Raman signals in two spectral regions at different stages of metal deposition,
the growth process was interrupted for the accumulation periods. All depositions took place at room temperature.

Previous atomic force microscopy (AFM), x-ray diffraction (XRD), and Raman spectroscopy investigations have shown that the 15 nm PTCDA and DiMe–PTCDI films consist of crystalline islands. While the PTCDA islands are closely packed the DiMe–PTCDI domains are elongated with large spaces between them.12

The UHV chamber is optically aligned with a Raman spectrometer, allowing in situ measurements to be performed. The Raman spectra were excited with the 2.54 eV line of an Ar⁺ laser that is located in the first absorption band of the PTCDA and DiMe–PTCDI yielding resonant Raman scattering. The scattered light is collected by a Dilor XY 800 triple monochromator with a multichannel charge coupled device detector. The spectral resolution was determined from the full width at half maximum (FWHM) of the laser line. The incident laser beam with the power about 100 mW was focused onto a spot having a diameter of 300 μm yielding a power density below the damage threshold of the absorbing molecular films (~100 kW/cm²).

Two polarization configurations were used. In the Porto notation \( z(x)z \) and \( z(y)z \) denote the cases when the incident electric field vector of scattered light is parallel/ perpendicular to that of the analyzed light (parallel/crossed polarization configuration). Here the \( x \) and \( y \) axes coincide with the substrate axes: \( x = x_s = [011], y = y_s = [0\overline{1}1] \).

Frequency calculations for single molecules were performed with the B3LYP functional and the 3-21G basis set using the GAUSSIAN'98 package.13 A mode assignment is made according to reference.14 In addition, the frequency spectrum of the complex In₃PTCD was calculated with the same functional and the basis set LANL2DZ which takes into account possible relativistic effects due to the presence of the metal atoms.13 The In atoms were assumed to interact with the PTCDA molecule via the O atoms in the anhydride groups, according to Ref. 10.

III. RESULTS AND DISCUSSION

Metal deposition onto 15 nm thick films of PTCDA and DiMe–PTCDI was monitored in two spectral regions: below 600 cm⁻¹ where the interest is focused on the phonons and breathing modes, and between 1200 and 1700 cm⁻¹ where the C–H deformations and C–C and C–O stretch modes are located. It must be noted that the latter is the only region where a sufficient signal was obtained from the ML organic coverage.

In Figs. 1(a) and 2 the spectra of 15 nm films of PTCDA and DiMe–PTCDI, respectively, are shown for metal coverages of 43 and 26 nm, respectively. The signal of PTCDA layers is equally strong in parallel and crossed polarization geometries, due to the almost orthogonal arrangement of the molecules in the unit cell. Therefore the latter configuration was chosen for presentation. The spectra in the low frequency windows are normalized to the height of the breathing modes at 233 and 221 cm⁻¹ in PTCDA and DiMe–PTCDI, respectively. The normalization of the high frequency region is performed with respect to the C–C stretch modes (1572 and 1570 cm⁻¹, respectively). Figure 1(b) displays the normalized spectra of ML PTCDA films covered with 7 nm Ag or In.

The Raman spectra of the 15 nm thick PTCDA and DiMe–PTCDI films are similar to those obtained from thicker films or molecular crystals. The Raman spectra of the
ML organic films show some differences compared to the “bulk” signal. These differences are discussed in detail for the case of PTCDA in Ref. 15 and attributed to contributions from molecules interacting with surface defects to the scattering process. The chemical treatment followed by annealing of the GaAs surfaces leads to $2\times1$ reconstructed S-terminated surfaces, the quality of which has been proven by the observation of a $2\times1$ low energy electron diffraction pattern.\(^9\) Moreover, x-ray reflectivity studies showed a roughness in the range of 1–2 nm at the PTCDA/S-GaAs interface.\(^16\) Therefore no direct effect of the interface roughness on the Raman signal can be evidenced for the system under investigation.

The deposition of Ag and In onto PTCDA leads to the appearance of the $B_{1u}$ band at 1243 cm$^{-1}$ and the increase in the relative intensity of the $B_{3g}$ mode at 1338 cm$^{-1}$ while the band at 1606 cm$^{-1}$ is not well resolved [Fig. 1(a)]. These bands are strongly enhanced compared to the $A_g$ modes during the Ag deposition onto the ML PTCDA film [Fig. 1(b)], therefore they can be considered as the signature of the “first layer effect,” i.e., of the molecules having direct contact with Ag. The band at 1338 cm$^{-1}$ was identified in Ref. 17 to be a $B_{3g}$ band based on its frequency and intensity in the crystal spectra, while the band 1292 cm$^{-1}$ is likely to be a shifted variant of the C–H deformation $A_g$ mode at 1303 cm$^{-1}$ in the single crystal.\(^13\) However, an infrared $B_{2u}$ character of this mode cannot be excluded. The other bands correspond to modes that normally show infrared activity. In Ref. 18 the observed breakdown of the Raman-infrared selection rules was proposed to originate from a weak charge transfer between the molecules and the metal surface mediated by molecular vibrations, according to a “ground state charge transfer” model proposed by Lippitsch.\(^19\) Interestingly, the same modes are also activated in the spectra of PTCDA monolayer when covered with indium, only with different relative intensities. This reflects the same type of weak interfacial interaction based on fractional charge transfer. The PES data of Kera et al.\(^10\) and Hirose et al. indicate the appearance of a state in the original HOMO–LUMO gap of PTCDA upon In deposition. Kera et al. attribute the new state as a mixed state consisting of $C2p_z$, $O2p_z$, and $In5p_z$ wave functions as a result of the formation of In$_4$PTCDA complex. DFT calculations for the In$_4$PTCDA complex showed that the LUMO +2 and LUMO of the pristine PTCDA correspond to HOMO and HOMO-1 in In$_4$PTCDA which was related to the electron transfer from In to PTCDA.\(^10\)

In order to assess the effect of a metal-PTCDA complex formation on the vibrational frequencies theoretical calculations were performed as described in Sec. II. The optimized geometry, the electronic levels and the charge distribution over the complex are similar to those reported in Ref. 10. Figure 3 shows the spectrum of a PTCDA single crystal to-

![Figure 2](image2.png)

**FIG. 2.** Raman spectra of 15 nm thick DiMe–PTCDI films covered with 26 nm Ag or In (a) and ML DiMe–PTCDI films covered with 7 nm Ag or In (b). The spectra were recorded in the $z(xx)\parallel$ polarization configuration.

![Figure 3](image3.png)

**FIG. 3.** Raman spectrum of a PTCDA crystal along with calculated frequencies for a single molecule (rhombus) and for a In$_4$PTCDA complex (triangles).
gether with the calculated frequencies for a single PTCDA molecule (rhombus) and for an In$_4$PTCDA complex (triangles). The most dramatic effect of the complex formation resides in the twofold splitting of the breathing mode at 233 cm$^{-1}$ (see the elongation patterns in Fig. 2). A first component originates from a breathing of the whole complex and the significant increment of mass compared to the single PTCDA molecule results in a dramatic shift towards lower frequencies (110 cm$^{-1}$). For the second component the In atoms are fixed and constrain the breathing of the PTCDA molecule increasing its frequency to 299 cm$^{-1}$. In the experimental spectrum [Fig. 1(a)] of the In$_4$(43 nm)/PTCDA(15 nm) heterostructure, the molecular breathing mode is still observed at 233 cm$^{-1}$, ruling out the possibility of this chemical reaction. This conclusion is further supported by infrared spectroscopy studies. It can be observed in Fig. 4 that the frequency positions in the reflectance spectrum of a In$_4$(15 nm)/PTCDA(15 nm)/GaAs system coincide with those in the spectrum of a 130 nm PTCDA film on S–GaAs. Here the C=O vibrations around 1700 cm$^{-1}$ deserve attention since they should be significantly affected by the presence of an In$_4$PTCDA complex. However, their positions are preserved in the spectrum. The discrepancy between results of this study and those of Ref. 10 may be explained by different preparation conditions: here the organic and the metal films were deposited at RT, while in Ref. 10 the substrate was kept at 100 °C during the PTCDA and In deposition.

Besides the occurrence of “first layer” related modes in the spectrum of Ag and In on 15 nm thick PTCDA films the totally symmetric modes are also enhanced, as shown by the normalization factors in Fig. 1(a). The latter effect originates from the coupling between the incident and scattered radiation with localized and/or collective plasmon resonances in the metal film. This long range electromagnetic mechanism usually implies a high roughness of the metal film and induces the enhancement of Raman signal from molecules in the molecular films up to several nm away from the metal surface.

In the spectra of Ag and In on 15 nm DiMe–PTCDI films again the “first layer effect” and the long range electromagnetic mechanisms contribute to the total signal enhancement. The former leads to the enhancement of the modes at 1246 and 1606 cm$^{-1}$. The Raman active vibrations related to C=O bonds (1610 and 1687 cm$^{-1}$) as well as the breathing mode at 221 cm$^{-1}$ survive with increasing Ag coverage. Thus a chemical reaction between the Ag and the O atoms of DiMe–PTCDI molecules can again be ruled out.

It has been shown that the spectra of metal/organic (15 nm) heterostructures consist of a superposition of signals from molecules in intimate contact and molecules having no interaction with the metal interface. The latter class of molecules are molecules in the “bulk” of the organic islands and their Raman scattering can only be enhanced via the long range electromagnetic mechanism. Since the totally symmetric $A_g$ modes are enhanced via dipolar resonances, their intensity is very sensitive to the morphology of the metal film. On the other hand, the intensity of the $B_{1g}$ modes enhanced via the “first layer effect” relative to the $A_g$ modes could give an estimate on the fraction of molecules in contact with metal and hence of the metal diffusion into the organic films.

For a quantitative determination of the enhancement factors curve fitting of each set of spectra recorded during the silver and indium onto PTCDA and DiMe–PTCDI deposition was performed using Lorentzian peaks. The dependence of relative area on the Ag and In coverage is plotted in Figs. 5(a) and 5(b) for three bands of each organic material. The relative intensities were calculated by dividing the intensities in the spectra at a given coverage by the initial intensities in the spectrum where the mode occurs for the first time. For example, the reference spectrum for the Raman band at 1572 cm$^{-1}$ is that of the pure organic film, while the reference spectrum for the bands at 1243 and 1606 cm$^{-1}$ is that taken after the first Ag deposition.

The overall signal initially increases reflecting an increase in number and size of metal clusters with their plasmon energy approaching the energy of the laser electromagnetic field. The maximum enhancement of PTCDA modes for the Ag/PTCDA(15 nm) system is observed around 11 nm nominal Ag coverage [Fig. 5(a)], probably corresponding to the optimum cluster size for the dipolar plasmon resonance or to the initiation of percolation between clusters. The In film

**Fig. 4.** Infrared reflectance spectra of a 15 nm In/(15 nm) PTCDA/S–GaAs structure and of a 15 nm PTCDA film on S-GaAs substrate.

**Fig. 5.** Enhancement factors of several internal modes of PTCDA (left-hand side) and DiMe–PTCDI (right-hand side) as a function of the metal coverage: Ag (upper graphs) and In (lower graphs).
thicknesses yielding the maximum enhancement for PTCDA and DiMe–PTCDI films are 26 and 5 nm, respectively. A further increase in the metal thickness leads to increasing size of the metal clusters associated with decreasing strength of the plasmon coupling with the incident and scattered radiation. The absorption in a closed metal film also plays an important role in decreasing the Raman signal for higher nominal coverages. However, even for a metal coverage of 43 nm the signal from PTCDA and DiMe–PTCDI internal modes is still observed, with higher intensity compared to the pure organic film. Noteworthy, for Ag deposition onto DiMe–PTCDI no saturation of the signal intensity was observed up to a coverage of 263 nm. The observation of internal molecular modes in all the metal/organic heterostructures presented here for such high metal coverages is surprising considering that the light penetration depth in Ag and In is 13.6 and 8 nm, respectively (at 2.54 eV). Brouers et al. showed that giant Raman scattering can be observed for any kind of percolating systems, even for the case of metals which are characterized by a low light penetration depth in the form of a closed film. The prime candidates are systems containing strongly elongated metal inclusions, a condition fulfilled by the present metal films, as it can be observed in the AFM images in Fig. 6.

Two types of roughness can be distinguished in the 263 nm Ag film on DiMe–PTCDI. The high columnar Ag clusters (Fig. 6) preserve the shape of DiMe–PTCDI islands in low coverage films (see Ref. 12) therefore it can be assumed that these structures cover the organic islands. Smaller structures with lateral size of 50–100 nm can be observed on top of the large Ag islands as well as on the metal accumulated between the organic islands. These observations are in agreement with previous XRD results revealing that the Ag films grown on 15 nm thick DiMe–PTCDI films have a polycrystalline structure. In the same work it was found that the Ag films grown on PTCDI are predominantly Ag (111). Such a difference in morphology may explain the lower enhancement factors observed for PTCDI compared to DiMe–PTCDI.

Upon increasing the metal coverage the intensity of the vibrational modes of DiMe–PTCDI increases more in the crossed compared to the parallel polarization configuration and for a certain coverage the intensity becomes equal. The observed loss of the polarization dependence can be explained by the depolarization of light due to multiple elastic scattering by metal clusters before and after the Raman scattering process on molecules. This effect provides an additional argument for the rough morphology of the metal layers.

A qualitative estimation of the diffusion of the metal into the organic crystalline islands in the 15 nm organic interlayer can be made from the intensities of the $B_u$ modes enhanced via the “first layer effect” relative to the $A_g$ modes enhanced via the long range electromagnetic effect. In the case of Ag/PTCDI and Ag/DiMe–PTCDI the intensity is low, indicating that only few molecules have intimate contact with Ag. This leads to the conclusion that the Ag atoms do not diffuse into the PTCDI crystallites. On the other hand, the spectra of In(15 nm)/PTCDI the $B_u$ bands are stronger compared to the $A_g$ modes reflecting a large number of PTCDI molecules that experience the first layer effect and hence a strong diffusion of In into the PTCDI islands, in agreement with the previous PES results in Refs. 2 and 10. In/(15 nm)DiMe–PTCDI represent an intermediate case between Ag/PTCDI and In/PTCDI.

The ratio between the area of the $B_u$ mode at 1243 cm$^{-1}$ (1246 cm$^{-1}$) and that of the $A_g$ mode at 1572 cm$^{-1}$ (1570 cm$^{-1}$) in PTCDI(DiMe–PTCDI) is shown as a function of metal thickness in Fig. 7. In the case of Ag/DiMe–PTCDI the maximum value is observed for the first Ag deposition, i.e., 0.4 nm Ag, whereas for PTCDI it increases up to a 1.4 nm nominal coverage of Ag. For In deposition onto both organic layers this ratio reveals a saturation tendency only above 15 nm nominal In coverage. It is proposed that a maximum in the above defined ratio can be directly related to the metal diffusion length in the organic film. Thus the Ag atoms arriving at the organic film surface diffuse into the PTCDI or DiMe–PTCDI islands up to a nominal Ag coverage of 1.4 and 0.4 nm, respectively.

A complementary means to check whether the metal at-

![Fig. 6](Image 76x546 to 273x743)

**Fig. 6.** AFM image of Ag(263 nm)/DiMe–PTCDI(15 nm)/S–GaAs(100).

![Fig. 7](Image 336x627 to 540x743)

**Fig. 7.** Ratio between area of the $B_u$ mode (1243 cm$^{-1}$ in PTCDI and 1246 cm$^{-1}$ in DiMe–PTCDI) and of the C–C stretch $A_g$ mode (1572 cm$^{-1}$ in PTCDI and 1570 cm$^{-1}$ in DiMe–PTCDI).
omns reach the GaAs surface is to monitor the ratio between the area of the GaAs longitudinal optical (LO) phonon at 292 cm$^{-1}$ and that of the coupled plasmon-longitudinal-optical phonon (PLP) band at 268.5 cm$^{-1}$ which is related to the electronic band bending at the GaAs surface. In the case of the lowest coverages of PTCDA or DiMe–PTCDI the band bending increases in the initial stages of the Ag and In deposition, indicating that the presence of such a thin organic interlayer is not able to prevent the penetration of Ag atoms and their reaction with the substrate top layers. An increase in the GaAs band bending is also observed upon the deposition of 0.4 nm metal onto the 15 nm layers of organic films. Considering the low diffusion of Ag into the organic islands, the metal atoms can only react with the substrate in the free space between the organic islands. The changes are more significant in the DiMe–PTCDI case due to the larger voids between molecular islands compared to PTCDA.

**IV. SUMMARY**

Ag and In deposition onto RT grown PTCDA and DiMe–PTCDI films on S–GaAs(100):2 × 1 was characterized in situ by Raman spectroscopy. The interactions at the metal/organic interface were probed by depositing the metal onto ML coverages of organic molecules. A process of dynamical fractional charge transfer modulated by molecular vibrations is proposed to be responsible for the enhancement of modes and for the breakdown of selection rules in the spectra of metal/(ML) organic heterostructures. In metal/organic heterostructures with 15 nm thick organic films the enhancement factors of the signal from the organic molecular reflect a high level of roughness of the metal overlayer. Moreover, the intensity of the normally infrared active modes relative to the Raman modes provides information on the metal diffusion depth in the organic films.

**ACKNOWLEDGMENTS**

This work was supported by the EU funded Human Potential Research Training Network DIODE (Contract No. HPRN-CT-1999-00164) and by the Deutsche Forschungsgemeinschaft within the framework of OFET (Project No. SPP 1121/Za146/4-2).

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