

Interface formation of Mg with DiMePTCDI studied by Raman spectroscopy

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Metal/organic interfaces play an important role in the performance of organic based devices. In this work the interface formation between Mg and N,N'-DiMethyl-3,4,9,10-Perylene Tetra Carboxylic DiImide (DiMePTCDI) films grown on sulphur-passivated GaAs (100) substrates is investigated *in situ* by Raman spectroscopy. The Raman spectra are taken in a backscattering geometry at room temperature under resonance conditions with the 488 nm (2.54 eV) Ar⁺ laser line. They reveal that when Mg is deposited onto a 15 nm DiMePTCDI layer the external phonon modes are preserved up to large metal coverages. Since these modes are a fingerprint of the molecular crystal, their preservation indicates a low diffusion of Mg into the DiMePTCDI layer. Concerning the internal molecular modes, the Mg deposition induces a breakdown of selection rules which is proposed to originate from a dynamical charge transfer between the DiMePTCDI molecules and the metal. Above 0.3 nm nominal thickness of Mg the line-shape of the molecular breathing mode at 221 cm⁻¹ develops an asymmetric tail towards higher frequencies. A similar effect is observed for the bands that occur at 1291 cm⁻¹ and 1606 cm⁻¹ but the asymmetry appears at the low frequency side. This line-shape asymmetry is likely to be related to a Fano resonant coupling between the molecular vibrational modes and the electronic continuum of states of metallic clusters formed above 0.3 nm Mg coverage.

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1 Introduction

Organic materials are well-suited for applications in organic based electronic devices like organic field effect transistors, organic light emitting diodes and organic solar cells [1,2,3,4,5]. The delocalised character of the π orbitals of the aromatic molecules make them suitable for charge transport. The nature of these materials allows lower-cost electronics compared to those based on the inorganic materials and even bendable plastic electronics can be achieved.

The understanding of the interface formation between the organic layers and the electrodes is necessary to optimize the performance of working devices [6]. In this work the investigation of the metal/organic interface formation is performed using Raman spectroscopy, which probes the inelastic light scattering by molecular vibrations and thereby provides information about the normal mode frequencies of a molecule. Thus the vibrational spectrum is a characteristic fingerprint of the investigated system. Information concerning the chemical identity, charge states, processes at interfaces and structural order in organic materials, can be identified using this spectroscopic technique [7,8,9,10].

Here, the chemical aspects of the interface formation between magnesium and a molecule from the class of the perylene derivatives, namely N,N'-DiMethyl-3,4,9,10-Perylene Tetra Carboxylic DiImide (DiMePTCDI) is investigated. Further information on the diffusion of the metal atoms into the molecular

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The activation of modes with lower symmetry was also observed during the deposition of other metals, like Ag and In onto DiMePTCDI [7]. This is a well known effect for molecules in contact with metal surfaces [13]. It can be either induced by molecular deformation in the vicinity of an interface or by charge transfer processes from the molecule into the metal or vice-versa.

In addition to the spectral changes discussed above the deposition of Mg up to a coverage of 21 nm leads to a decrease in the overall signal as reflected by the normalization factors in Fig. 1. The signal decrease is caused by the light attenuation in the metal overlayer. With increasing the Mg coverage above 21 nm, however, the intensity of all bands increases again. The maximum enhancement factor relative to the intensity in the spectrum of the bare organic film is observed for the C-C stretching mode at 1570 cm^{-1} and it amounts to 7.6 for a Mg coverage of 122 nm. The increase of the Raman signal of the organic layer upon metal deposition was also observed for In and Ag [7]. This effect occurs due to the enhancement of the electric field of the incoming and scattered radiation induced by plasmons that are resonantly excited by the electromagnetic radiation in the metal clusters. Therefore the enhancement of the Raman signal provides a clear proof for a high degree of roughness of the metal film.

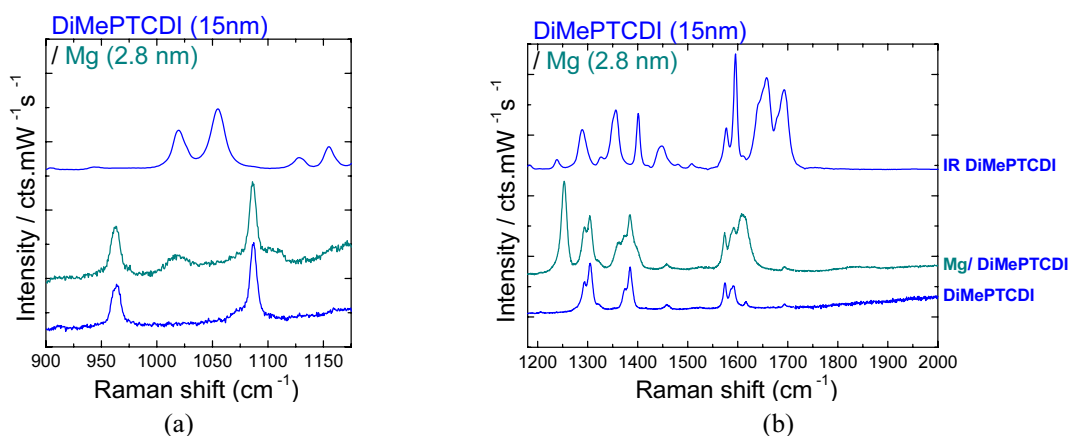


Fig. 2 Comparison between the Raman spectra of bare DiMePTCDI, Mg (2.8 nm)/DiMePTCDI and the IR spectra of the organic material.

Upon metal deposition up to 21 nm the external modes (phonons) below 120 cm^{-1} remain unchanged. Considering that the external modes are a signature of the organic layer crystallinity, their preservation indicates that the Mg atoms do not diffuse into the organic crystalline islands.

3.2 Coupling of vibrational modes and electronic excitations

Another modification induced by the metal deposition on the Raman spectra is an asymmetric broadening of the breathing mode at 221 cm^{-1} , and the modes at 1291 cm^{-1} and 1606 cm^{-1} .

Similar asymmetric line-shapes were observed for metal-doped fullerene films [14] and in the Raman spectra of metallic carbon nanotubes [15,16]. There it was suggested that the asymmetric line-shape can be fitted with a Breit-Wigner-Fano (BWF) function that accounts for a coupling between discrete phonons to an electronic continuum, a so called Fano resonance. Fano resonances were also observed in the Raman spectra of inorganic systems such as highly doped Si [17] or semiconductor superlattices [18,19]. The BWF function reads:

$$I(\omega) = I_0 \frac{1 + \left((\omega - \omega_{BWF}) / (q\Gamma) \right)^2}{1 + \left((\omega - \omega_{BWF}) / \Gamma \right)^2}, \quad (1)$$

This expression can be rewritten as: $I(\omega) = \tilde{I}_0 \frac{(q + \varepsilon)^2}{1 + \varepsilon^2}$, where $\varepsilon = \frac{\omega - \omega_{BWF}}{\Gamma}$ is the reduced energy with ω_{BWF} being the Breit-Wigner-Fano frequency and Γ the resonance width related to the phonon self energy when the interaction with the electronic continuum takes place. q is the asymmetry parameter and $(1/q)$ is proportional to the degree of coupling.

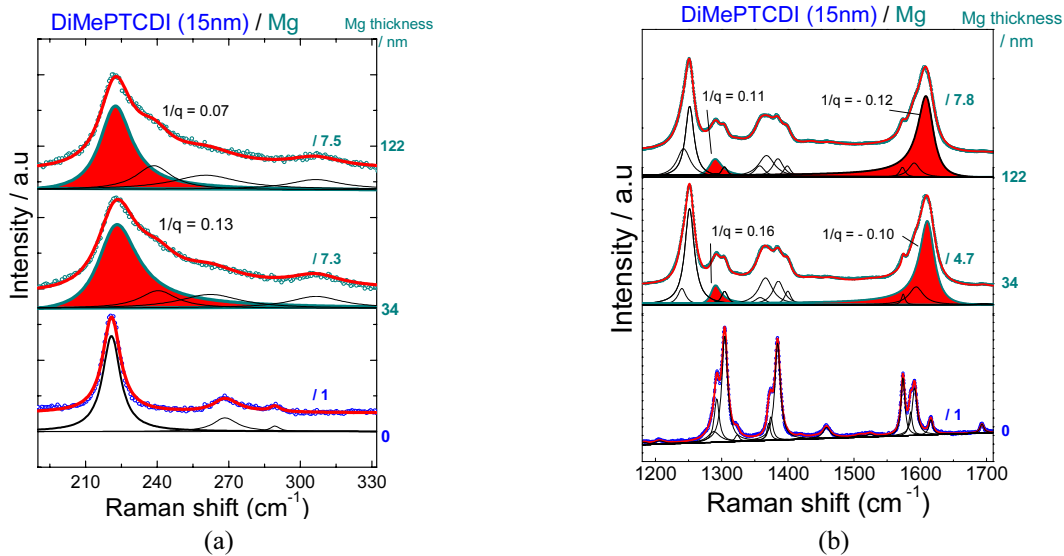


Fig. 3 Raman spectra of Mg / DiMePTCDI: from bottom to top: bare 15 nm DiMePTCDI covered with 34 nm Mg and 122 nm Mg. The experimental and fitted spectra are shown by symbols and thick lines, respectively. The peaks described with the BWF function in the case of Mg covered DiMePTCDI are represented by thick black lines.

Here the BWF function is employed for fitting the modes at 221 cm^{-1} , 1291 cm^{-1} and 1606 cm^{-1} . All other modes are fitted using lorentzian functions. Figure 3 shows from bottom to top experimental Raman spectra along with the fitting curves for bare DiMePTCDI (15nm), partial coverage of 34 nm Mg, and 122 nm Mg thickness. The absolute values of $(1/q)$ range from 0.07 to 0.16. For comparison, $(1/q)$ ranges from 0.18 to 0.27 for a band at 1543 cm^{-1} in the case of metallic carbon nanotubes [16]. The value of $(1/q)$ is influenced by the choice of the background. Therefore it is difficult to draw conclusions regarding changes in the degree of coupling with the increase in metal coverage. It must be noted that the asymmetry parameter of the band at 1606 cm^{-1} band is negative, while the other two BWF line-profiles are characterized by positive asymmetry parameters. According to reference [14] a negative/positive value of the coupling parameter indicates that the centre frequency of the continuum lies below/above the discrete mode frequency.

For an excitation energy of 2.54 eV the energy of the photons scattered by the molecular vibrations at 1291 cm^{-1} and 1606 cm^{-1} amounts to 2.38 eV and 2.34 eV, respectively. It must be noted that the band asymmetry occurs at metal coverages for which also the enhancement of the Raman signal due to dipolar plasmon resonances is observed. Therefore we propose that the origin of the observed BFW line-shapes is a coupling between the molecular electronic levels with the plasmons in the Mg clusters modulated by the molecular vibrations. Interestingly, the band at 221 cm^{-1} stems from a breathing vibration of the whole molecule and the band at 1606 cm^{-1} stems from a breathing mode with mainly C-C stretching character. Thus both involve the breathing of the carbon rings.

4 Conclusions

In this work the deposition of magnesium onto the perylene derivative DiMePTCDI was studied by means of in situ Raman spectroscopy. Besides the normally Raman-active internal molecular modes, additional features are induced in the spectra of the organic film by the presence of the metal. These modes are activated by a process of charge transfer at the interface between the molecules and magnesium. The bands at 221 cm^{-1} , 1291 cm^{-1} and 1606 cm^{-1} are broadened asymmetrically upon metal deposition and their line-shape is well described by a Breit-Wigner-Fano function. This effect is accompanied by an enhancement of the Raman signal intensity due to plasmon excitations in the metallic clusters. It is proposed that the BWF line-shapes originate from a coupling between the molecular electronic levels with the plasmons in the Mg clusters modulated by the molecular vibrations. The enhancement in the Raman signal is observed above 21 nm Mg coverage and reflects a high degree of roughness of the metal film.

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