Raman investigation of electric field induced molecular modifications in organic field effect transistors

Beynor Antonio Paez Sierra[1][2][*], Fredy Giovanni Mesa Rodríguez[3][**]

[1] Thin Films Group, Physics Department, Pontificia Universidad Javeriana. Bogotá, Colombia

[2] Institut für Physik, TU-Chemnitz, 09070 Chemnitz, Germany

[3] Universidad Libre, Departamento de Ciencias Básicas. Bogotá, Colombia

Abstract. The influence of external electric fields on the vibrational properties of Pentacene-based field effect transistors were investigated by Raman spectroscopy. The monitored Raman bands were in the range from $1100 \ \mathrm{cm}^{-1}$ to $1200 \ \mathrm{cm}^{-1}$, where a broad band is present and enhanced due to the external electric field. The process is modeled by density functional theory (DFT) at the B3LYP/3–21G level. Additionally, the relaxation of the Raman bands after the removal of the external field was determined from an exponential Debye like decay fitting to be approximately 94 min, this finding indicates that a long relaxation time ca. 8 h is required in order to recover the original structure. Experimentally and theoretically was demonstrated that the applied electric fields induce artificial traps in the organic layer mediated by charge carrier–dipole interaction.

Keywords: pentacene, Raman spectroscopy, organic transistors, DFT.

Resumen. La influencia del campo eléctrico externo sobre las propiedades de transistores de efecto de campo basados en el Pentaceno fueron investigadas a través de espectroscopia Raman. El monitoreo de las bandas Raman fue en el rango de $1100 \ \mathrm{cm}^{-1}$ a $1200 \ \mathrm{cm}^{-1}$, donde una banda

[*] Físico (1996: Tesis con mención meritoria) con Maestría (1999) y énfasis en energía solar. Doctorado en la Technische Universität Chemnitz Alemania (2008) con énfasis en electrónica orgánica, espectroscopia Raman, UV vis, infrarrojo, fotoluminiscencia, experto en el área experimental de investigación y desarrollo de dispositivos basados en nanofotónica y nanotecnología. Temas de interés: nanofotónica, sensórica, electrónica plástica molecular, energía solar, aplicaciones en la industria. `bpaez@javeriana.edu.co`

[**] Licenciado en Física (2003), Magister en Física (2006) y Doctor en Física (2010 con Tesis Doctoral Meritoria) énfasis en energía solar y física de semiconductores. Los resultados del trabajo de investigación y de docencia están reportados en 38 publicaciones nacionales e internacionales. Temas de interés: energía solar fotovoltaica, semiconductores, electrónica orgánica, espintrónica. `fredyg.mesar@unilibrebog.edu.co`

ancha está presente y mejorada debido al campo eléctrico externo. Este proceso es modelado a través de la Teoría de Densidad Funcional (DFT) a nivel B3LYP/3–21G. Adicionalmente, la relajación de las bandas Raman después de remover el campo externo fue determinado a partir de un ajuste del decaimiento exponencial de Debye aproximado en 94 min, indicando un largo tiempo de relajación. 8 horas son requeridas para retomar su estructura original. Experimentalmente y teóricamente fue demostrado que el campo eléctrico aplicado induce a trampas artificiales en la capa orgánica mediado por la interacción carga–dipolo.

Palabras Clave: pentaceno, espectroscopia Raman, transitores organicos, TDF.

1. Introduction

The advance of flexible electronics in recent years has made promising applications in electronic papers, radio–frequency identification (RFID) tags, and electronic signage etc. Therefore, organic electronic devices including organic light–emitting diodes (OLEDs) [1], organic thin–film transistors [2] and organic photovoltaic cells [3] have been investigated extensively because of their unique features such as low–temperature processing, low cost, light weight and mechanical flexibility. Today still is required a huge scientific investment to understand these materials. Some important issues to characterize the organic/inorganic or $organic_1$/$organic_2$ interfaces are trap and stress states [4]. Among the optical techniques, Raman spectroscopy allows one to derive detailed and specific information on a molecular level that other laser or electronic spectroscopic methods can provide only to a limited extent [5,6]. Raman spectroscopy is a non–destructive technique and requires minimal or no sample preparation. The vibrational spectrum is a fingerprint that belongs to a specific system. Therefore, chemical identity, reactivity, diffusion, charge states, phenomenology at interfaces, mechanical and electrical stress and many others are capable to be investigated by Raman spectroscopy [7,8]. Additionally, the vibrational investigation permits energetically to resolve fine–structure features, i.e. a 1000 cm^{-1} Raman shift corresponds to about 123.9 meV. Here the analysis resolves energies as better as 10 meV.

In addition, taking the advantage of Raman spectroscopy to detect charge states, it is worth to apply electric fields to the molecular structure. Therefore, charge displacement of the electrons in the outer shell of the atoms is promoted. The induced electronic rearrangement results in induced dipoles. Thus, shifts of the Raman bands, and/or modifications of the modes intensity [9], enhancement or quenching [10], alteration of the normal molecular absorption and distortion are observed. The changes produced by the electric field named electronic or geometric distortions are understood as symmetry breakdown of the molecule [11].

The paper is organized as follows. In section 2, the experimental procedure is described. In section 3, the theoretical simulation based on density functional theory of the molecular orbitals of a pentacene molecule under electric fields is

illustrated. Then, the combined electric and Raman measurement in a field effect transistor with pentacene as active layer is discussed. Finally, some concluding remarks are addressed.

2. Experimental

The OFET devices were fabricated using heavily doped p–type silicon substrates covered by a high quality thermally grown oxide with a thickness of about 150 nm acting as gate electrode and gate oxide, respectively. Afterwards, a thin Ni wetting layer of 5 nm was deposited onto the gate dielectric, and subsequently DC–sputtering of Au on top of it was done, resulting in an improved adhesion of the gold contacts on the SiO_2 substrate. The channel was patterned by UV contact–lithography and lift–off with ultrasonic agitation in acetone. The final geometry of the channels consists of a width and length of $W \times L = 180$ μm $\times$ 16 μm, respectively (cf. Figs. 1a-1b). As an organic material, Pentacene (Fig. 1c) purchased from Sigma Aldrich was thermally evaporated as received. The deposition rate was kept at about 1 Å/s and with a pressure of 2×10^{-6} mbar until the film reached a thickness of about 30 nm.

In order to prove the operation of the OFET a typical *ex situ* output drain–current characteristics for different gate voltages is displayed in fig. 1d, the measurement was performed at atmospheric and darkness conditions with a Keithley 238 high current source/measure unit controlled by a computer.

The Raman scanning spectroscopy (RSS) investigations were carried out in a fully atomized LabRAM ARAMIS spectrometer from Jobin Yvon HORIBA. The setup is equipped with three excitation laser lines provided by two solid state lasers (AlGa, Nd:YAG) and a gas laser (HeNe); a true confocal OLYMPUS microscope with various objectives, motorized x-y stage or sample holder with step resolution of about 500 nm, and motorized objective along the z–axis. Polarizers, knotch filters, turret with various gratings, and a high resolution Peltier–cooled CCD camera (256×1024 pixels). The OFET channel was analyzed in the back scattering configuration (cf. Figure 1a). A 632.8 nm (1.96 eV) light from the He-Ne laser and an intensity of 0.1 mW was used as excitation source. The light was focused on the sample through a ×100 objective resulting in a laser spot of ca. 1 μm diameter. The Raman setup is coupled to the drain–current voltage stage, for the combined Raman and electric field measurements, drain and source were in short circuit while the electric field was controlled by the gate terminal.

3. Influence of external electric fields on the molecular properties

3.1. Theoretical simulation

Influence of external electric fields on the molecular properties was theoretically simulated. Density functional theory (DFT) calculations were performed at the

(a)

(b)

(c) Pentacene $C_{22}H_{14}$

(d)
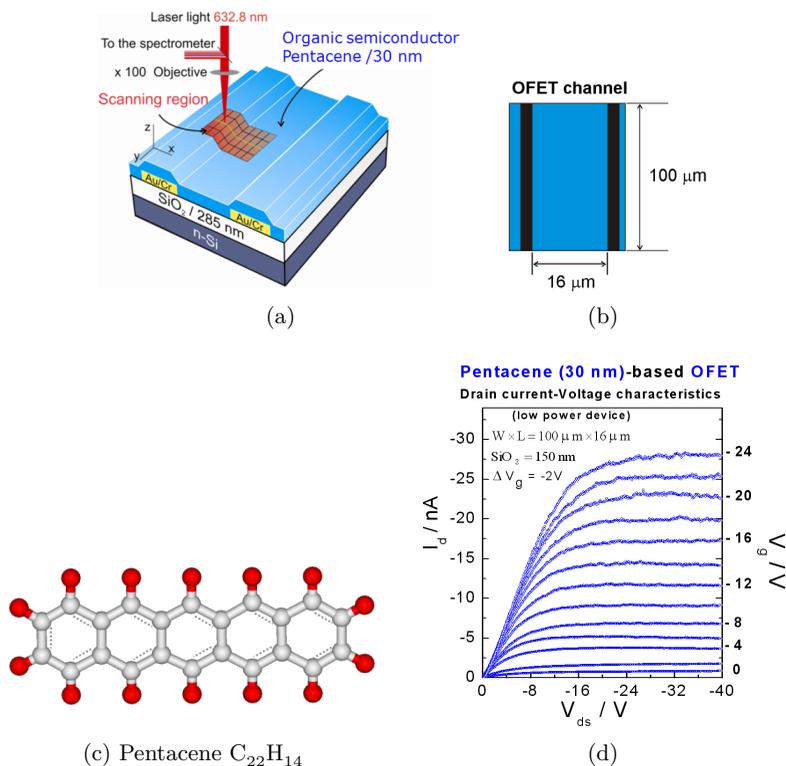
Fig. 1. Experimental (a) scheme of the organic field effect transistor (OFET) structure, (b) geometry of the channel. (c) Molecular structure of the organic semiconductor Pentacene ($C_{22}H_{14}$), and (d) typical *ex situ* output characteristics measured in darkness and under atmospheric conditions.

B3LYP/3–21G level in Gaussian 98. The simulation considers one pentancene molecule and exposed to electric fields. Figure 2 shows the orientation of the electric field and its effect on the molecular band–gap. It is found that the highest modification of the band–gap occurs when the electric field is applied along the y axis, which corresponds to the highest delocalization of the electronic cloud. According to previous results, the pentacene molecule grows perpendicular to the dielectric substrate i.e. with the "y–axis" perpendicular to the SiO_2 substrate. Therefore, significant changes for gate voltages are expected.

3.2. Experimental results: Raman spectroscopy measurements

In fig. 3a the experimental results of Raman spectroscopy with electric fields are shown. During the experiment the drain and source contacts were set in short circuit, while the gate contact was set to different voltages. The gate voltages
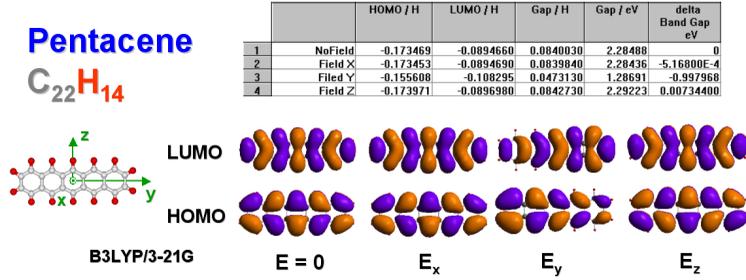
Fig. 2. DFT simulation of the influence of an applied electric field ($\mathbf{E}(o, x, y, z)$) on the molecular band gap and HOMO–LUMO states in Pentacene (H: Hatree = 27.2 eV).

were modified from 0 V and in steps of -4 V to a final voltage of -24 V. The most significant modification of the Raman bands was found to occur at the molecular in–plane C–C ring and C–H vibrations with Ag symmetry. For the experiment, the Raman intensity followed a square law dependence with the applied gate field; this is summarized in the correlated fitting illustrated in fig. 3b. Additionally, no changes in bands positions were observed. The Raman signal is dependent on the polarizability modulation of the investigated media. Consequently, one expected signature is the change of the Raman intensity (cf. Fig. 3)

(a)

(b)
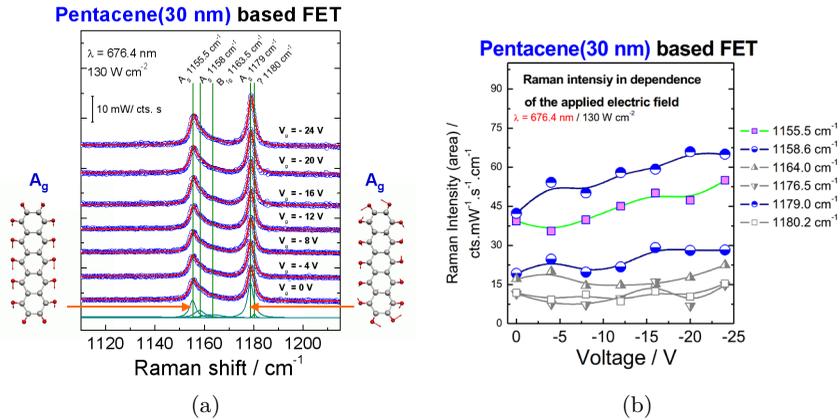
Fig. 3. Experimental measurements of the Raman bands in Pentacene (30 nm)/FET. (a) Raman spectra for different applied fields. (b) Correlated fitting of the Raman intensity as a function of the applied gate voltage.

The gradual enhancement of the Raman bands in response to the increase of the gate voltage provides an indication as to the formation of the conductive

channel in the pentacene–based FET. The experiment was then carried out by switching off the gate field and *in situ* monitoring of the vibrational bands relaxation, as illustrated in fig. 4. The timedecay constant was found to be about 94 min. This finding indicates that a long relaxation time ca. 8 h is required in order to recover the original structure.
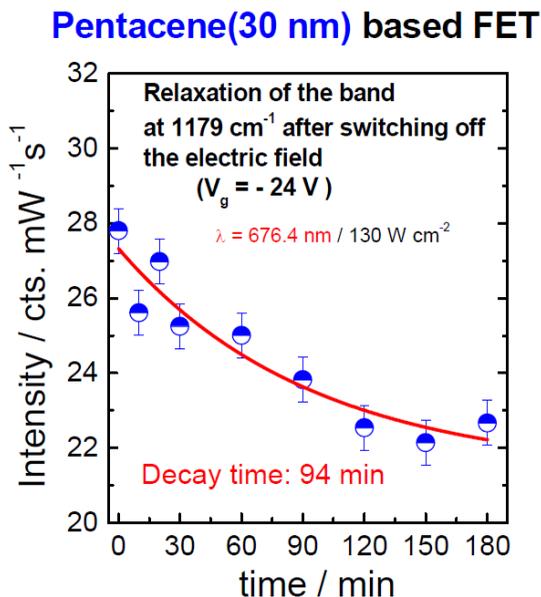
Fig. 4. Time decay of the Ag band at 1179 cm^{-1} after switching off the electric field.

4.   Conclusions

The influence of electric fields on molecular properties has been investigated by density functional theory (DFT), and experimentally with a combination of Raman spectroscopy and electrical characterization. The theoretical calculations showed an alteration of the molecular band–gap, vibrational and electronic states and removal of degeneracy when the investigated structure had a multiplicity of states at a given energy level.

The experimental results of Raman spectroscopy with electric fields in OFETs demonstrated a proportionality between the Raman signal and the applied field, which for pentacene (30 nm)–based FETs increases until applied voltages of about −20 V, followed by an attenuation for higher fields. The behavior suggests

considering competing phenomena between induced charge density and the creation of dipole–anion sites induced by the external field.

The subsequent vibrational measurements after switching–off the electric field indicate a dynamic relaxation of the Raman cross section with a time constant of about 94 min. The experiment predicted a long recovery time for the device.

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