Poster Session Afternoon (14h30 - 16h)

APPLICATIONS OF POLYMERIC MATERIALS AND ORGANIC ELECTRONIC DEVICES

[11/05/10 - P001]
Detection of VOCs using polythiophene derivative, Vanessa Cristina Gonçalves, Bruno Moser Nunes, Clarissa de Almeida Olivati, Depto. de Física - IGCE - UNESP
The growth of population and industrial development gave rise to unprecedented air pollution that can cause harm to humans and the environment. Efforts to reduce this pollution include recognition of the problem, collection of information, definition of sources and causes, and the selection and implementation of the appropriate solutions. Among the several types of conjugated polymers used in recent investigations, polythiophene and its derivatives have attracted considerable attention over the past 20 years due to their high mobility and other remarkable solid-state properties. They have potential applications in many fields, such as microelectronic devices, catalysts, organic field-effect transistors, chemical sensors and biosensors. In this work, we report on the fabrication of gas sensor arrays based on a conducting polymer poly(3-hexylthiophene)(P3HT) on an interdigitated electrode. This material was synthesized via oxidative polymerization using ferric trichloride. Under nitrogen atmosphere the monomer were dissolved in nitromethane and solid ferric chloride was added quickly to the mixture by a powder addition funnel under magnetic stirring. The response characteristics of the micro gas sensor films were then investigated against various test gases. Spin-coated (15mg/mL) of P3HT were deposited onto a glass substrate coated with the interdigitated chromium-gold array. Patterned Au electrodes were prepared by photolithography, where 25 pairs of lines act as electrode contacts. The length of the electrodes, their thickness and the distance between them are 800µm, 100µm and 100µm, respectively. The devices were characterized by measuring the current vs. voltage and current vs. time with applied voltage. The sensor were exposed to the different VOCs (volatile organic compounds) as, n-hexane, toluene, chloroform, dichloromethane, methanol and tetrahydrofuran, it was developed a system of flow atmosphere and "static"atmosphere, at room temperature. Prior to data acquisition the system of flow atmosphere and "static"atmosphere, methanol and tetrahydrofuran, it was developed a system to reach a stable reading. The sensors present a good response and sensitivity to the vapor gases tested. The behavior of the sensor in the presence of THF shows the best results when compared to the other ones (sensitivity and repeatability).

Acknowledgments: FAPESP and CNPq/INEO (Brazil), and are grateful to LNLS (Brazil) for providing interdigitated electrodes (project LMF 7832).

[11/05/10 - P002]
Fabrication of optical active polymeric microstructures connected with glass nanofibers, Vinicius Tribuzi, Daniel S. Corrêa, Cleber Renato Mendonça, USP - SP - Brasil
In this work we used femtosecond laser pulses to fabricate polymeric structures at microscopic scale by using the two-photon absorption induced polymerization. Due to the spatial confinement of the polymerization, provided by the two-photon absorption, this method allows for the fabrication of complex three-dimensional microstructures with high resolution, aiming at several technological applications, from photonic devices to biology. The resin we used is composed by two three-acrylic resins and the photoinitiator Lucirin TPO-L. With the developed apparatus we were able to fabricate microstructures as small as 6 µm with good spatial resolution. We also fabricated optical active microstructures by using doped samples. The microfabrication was carried out in the acrylic resins doped with Rodamine B, exhibiting, consequently, fluorescence when excited with light at 540 nm. Scanning Electron Microscopy (SEM) images show that doped microstructures show the same structural properties as the undoped ones. In order to optically connect these microstructures with external sources of excitation, such as laser beam, we developed an apparatus for the fabrication of glass nanofibers. We used a microscope objective lens to couple light (532 nm) into the macroscopic end of the taper. By using a micromanipulator on the taper we were able to manipulate and observe the fluorescence of individual microstructures.

[11/05/10 - P003]
Incorporation of renewable energy in the transport sector can effectively prevent disasters due to global warming in the future and the existence of energy crisis caused by large consumption of oil-based fuels. In this sense, lignocellulose is a potential source of biofuels such as bioethanol. Sugarcane bagasse is particularly suitable for this purpose, since it is available in large quantities as a residue of ethanol industry. Multi-enzyme complexes have the ability to catalyze the hydrolysis of cellulose. Efficiency of biomass bioconversion into fermentable sugars depends on the cellulose fiber structure that is exposed to the enzymatic activity. In this work we have succeed to attach a water soluble, highly fluorescent polymer to the cellulose fibers in order to visualize their microstructure after different types of pre-treatment (enzymatic and chemical). Here we have used a polyelectrolyte precursor of PPV (poly(p-phenylenevinylene)), the poly-(xylidenetetraydro-thiophenium chloride), PTH, a co-polymer that contains small conjugated units of the luminescent PPV and presents an exceptional photostability. High resolution confocal fluorescence and scanning electron microscopy was used for mapping micro enzymatic action and evaluating PTH incorporation. We will show that PTH diffuses along the fiber in few seconds and covers uniformly its internal and external microtubular wall. It also penetrates into submicron incrustations exposed by enzymes. The diffusion con-
Polymers can be produced on silicon chips to be coated with organic materials incorporating enzymes using the Langmuir-Blodgett or hybrid techniques. The experimental data will be compared with computational simulations to infer the influence of the film architecture and the materials used in the biosensors.


Acknowledgments: The authors are grateful to CNPq, CAPES, FAPESP, FINEP for the financial support.

Polymer humidity sensor, SUELEN DE CASTRO, RERO MARQUES RUBINGER, CARLA PATRÍCIA LACERDA RUBINGER, ANTONIO GERSO BERNARDO DA CRUZ, Universidade Federal de Juiz de Fora - MG, Brazil. ■ Commercial polystyrene was sulfonated with sulfonic acid groups to a degree of 22 mol%. Polystyrene and sulfonated polystyrene were analyzed with respect to its chemical and physical properties through titration, FT-IR, microprobe analysis and SEM. These techniques allowed us to determine the effectiveness of the sulfonation reaction and the changes of the physical properties it caused. Humidity sensors were obtained by dip coating a small plastic substrate with silk-screen fabricated interdigital carbon contacts. The composition of the ink as well as the contact matrix was designed to maximize the circuit response, i.e., by controlling the distance between contacts and the length and width of the contact matrix. The sensor impedance was measured by using a 1 kHz and 100 Hz LCR meter and compared to a commercial handheld humidity sensor in order to obtain a transfer function between the impedance and the environmental humidity. In order to obtain a wide range of environmental humidity we developed a chamber to mix dry and humid flowing air. Dry air was generated by flowing air through a silica gel recipient while humid air was generated by flowing air through a porous element inside a bottle filled with distilled water. This chamber can be hermetically isolated from the external environment and the humid/dry air flow ratio was controlled manually by using two faucets. The experimental results turn the sulfonated polystyrene into a very promising material for the fabrication of inexpensive humidity sensors with similar characteristics to commercially available sensors.

Theoretical aspects of field effect devices for applications in biosensors, M. A. MOURA DE SOUSA, J. R. SIQUEIRA JR, O. N. DE OLIVEIRA JR, IFSC - USP. ■ Field effect devices (FEDs) have been increasingly used as a platform for biosensors, in which phenomena of semiconductor physics such as the dependence of the capacitance on the applied potential in a MIS (Metal-Insulator-Semiconductor) capacitor are exploited. For the biosensors, in particular, enzymatic reactions release hydrogen ions that affect the electric potential at the electrode-oxide interface. This change in potential generates charge carriers in p-type semiconductors, thus creating a space charge region which modifies the device capacitance that is inversely proportional to the width of the depletion region. In order to understand the charge transport, we shall employ impedance spectroscopy measurements as the analysis of the data may allow one to distinguish between interface and bulk effects. The devices will be produced on silicon chips to be coated with organic or hybrid materials incorporating enzymes using the Layer-by-layer (LBL) or the Langmuir-Blodgett (LB) techniques. The experimental data will be compared with computational simulations to infer the influence of the film architecture and the materials used in the biosensors.

Acknowledgments: The authors are grateful to CNPq, CAPES, FAPESP, FINEP for the financial support.
Fabrication of multi-doped microstructures by two-photon absorption photopolymerization.,

A. J. G. Otuka, V. Tribuzi, D. S. Corrêa, C. R. Mendonça, Instituto de Física de São Carlos - Universidade de São Paulo - Brasil

The two-photon absorption polymerization technique allows the fabrication of complex three-dimensional microstructures with high spatial resolution. In this technique, a femtosecond laser beam (Ti:sapphire laser, 780nm, 40fs) is focused through a microscope objective in the volume of polymeric resin (monomer) containing a photoinitiator (organic compound responsible for initiating the polymerization process). The quadratic dependence on the intensity exhibited by the two-photon absorption allows the confinement of excitation to the focal volume, giving high spatial location of this manufacturing technique. The doping of the microstructures is extremely important because it allows the fabrication of devices with specific features. Methods for doping such microstructures have been recently developed aiming at application in optics, photonics and biology. Despite the recent advances in the doping of microstructures fabricated by two-photon polymerization, there are still no methods allowing the doping of microstructures with more than one organic compounds (dopant).

In this work, we developed a method for fabricating microstructures, by two-photon absorption polymerization that can be selectively doped with distinct organic fluorescent probes. The opto-mechanical system, the computer interface, as well as doping strategies, necessary to develop the multi-doped microstructure, have been implemented. The fabricated microstructures were characterized with scanning electron microscopy and fluorescent microscopy.

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Gamma radiation dosimetry using nanostructured polymer.,

Marcus Vinicius Gonçalves Vismara, Carlos Frederico de Oliveira Graeff, Universidade Estadual Paulista - UNESP - Bauru

High-energy electromagnetic radiation has practical applications in different industrial and medical areas. For instance, gamma rays are used for food sterilization, cancer treatment and for checking the structural integrity of large metallic pieces (gammagraphy). Such ionizing radiations are highly penetrating and can break chemical bonds and generate free-radicals when interacting with mater. This has several implications to human health as it can lead to premature elderly, genetic mutation, cancer or even death, depending on the dose of absorbed radiation. Therefore it is imperative that its use be properly controlled such that exact doses are applied.

In this work, the effect of gamma irradiation on MEH-PPV and nanostructured polymer (Pt-DEBP) was studied. Samples for ionizing radiation exposure were prepared in solution form in glass vials of 4ml (3cm height and 0.6 cm outer diameter) and hermetically closed with a solvent resistant plastic cap. The polymers have been dissolved in chloroform, when concentrations varying from 0.005 mg/ml to 0.1 mg/ml. Before and after irradiation, samples were stored in the dark inside a fridge, to minimize possible photo-oxidation or solvent evaporation. Irradiations were performed at the Hospital das Clínicas of UNESP (Botucatu) using a 60 Co cobalt unit (CGR model Alcyon II) at a dose rate of 168,50 cGy/min. Samples were irradiated between two poly(methyl methacrylate) (PMMA) plates (0.44 cm thick each) to allow correct electronic equilibrium for the 1.25 MeV gamma ray photons. Source size was 30 cm x 30 cm and the sample surface was at 80 cm from the source. Exposure time was varied to span the radiation dose from 10 cGy up to 30Gy. Optical absorption measurements in the UV-vis were made with a Shimadzu UVmini 1240 spectrophotometer.

As expected from previous reports (SILVA, Appl. Phys. Lett. 86, 131902 (2005)), the absorption spectrum of MEH-PPV showed shifts to the blue and has a decreased intensity. The Pt-DEBP showed the same general behavior. The results strongly indicate that the observed changes in optical properties of these polymers in response to gamma irradiation results from an indirect path where free radicals formed by the radiolysis of the solvent react with the polymer chain.

The results indicate that Pt-DEBP has a good potential for low dose dosimetric applications when compared with MEH-PPV results. However, further studies are being made to understand the gamma radiation effects in the polymer chain.
acterization of 6 different devices at the same time, using a LCR meter and polymeric sensors (PVA, PVAC, PMMA) which act as a template to different nanocomposites of polypyrrole/ gold nanoparticles. Results of electrical response relative to progressive introduction of acetic acid into the commercial wine will be analyzed as a way to detect the operational limit to the developed experimental setup.

[11/05/10 - P010]
Synthesis and electrical characterization of methanol sensors, Helinando P. De Oliveira, Ginneton F. Tavares, Colegiado de Pós-Graduação em Ciência dos Materiais, Universidade Federal do Vale do São Francisco ■ In this work, gold nanoparticles-polypyrrole (AuNPs-PPy) hybrid composites were manufactured by chemical polymerization of pyrrole monomer on the surface of metal nanoparticles and, subsequently, incorporated in poly(vinyl alcohol) (PVA) matrix to be exploited in sensing technologies for the detection and identification of methanol in mixtures with ethanol. The concentration of oxidant agent was optimized to maximize the sensitivity of sensors, allowing the determination of relative concentration of methanol molecules in binary mixture of methanol/ethanol based on the electrical response of sensor. The electrical impedance spectroscopy was used to characterize the interfacial processes of matrix/ volatile, allowing that processes such as electrical transport and polarization can be conveniently mapped, since in the range of frequencies from 1Hz to 1MHz it is possible to analyze the response of free and bounded charges. The results indicate that the sensitivity of sensors varies directly with dielectric constant of volatile organic compounds, indicating that dipolar orientation is affected by the progressive insertion of volatile molecules in the structure of polymeric matrices. We must notice that swollen processes are minimized to these systems, since the electrical response is dominantly positive (increase in the conductivity), in an indication that new conducting paths are generated by the introduction of molecules into the matrix, characterizing a reversible process.

[11/05/10 - P011]
A chemometric study about the interactions between polypyrrole nanocomposites and amphiphilic block copolymers of poly(ethylene)-bpoly(ethylene oxide), Helinando P. De Oliveira, Colegiado de Pós-Graduação em Ciência dos Materiais, Universidade Federal do Vale do São Francisco, Jacques Riemont, Clara Nogueiras, Universidade de La Habana, Rubén Sánchez, Universidade Estadual do Norte Fluminense ■ In this work we analyze the influence of amphiphilic block copolymers of poly(ethylene)-bpoly(ethylene oxide) (PE-b-PEO) on the structure of nanocomposites of polypyrrole and gold nanoparticles (PPy/ AuNPs), with the aim to elevate the surface area of mixed samples. In this direction, we used a chemometric study in which the concentration of both polymers is varied. The progressive introduction of PE-b-PEO into the nanocomposites is characterized from the analysis of the electrical impedance of colloids, the measurement of size of particles, absorbance in the UV-vis region and the TEM microscopies. The results indicate that at optimized concentrations it is possible to obtain organic cylindrical structures connected by gold nanoparticles. In this situation a reduction in the state of aggregation is observed, which act as a strong indication that new current pathways are created in the process of interaction between aggregates and the PE-b-PEO copolymers, promoting the minimization in the impedance levels of colloidal dispersion. The appropriate ratio of PE-b-PEO/ PPy improves the porosity of nanocomposites, optimizing the selectivity of devices applied as active cells in electronic nose systems. At present, work in our group is directed towards the application of these systems in the direction to characterize the contamination of wines from the progressive insertion of acetic acid.

[11/05/10 - P012]
High-energy x-ray detection using organic luminescent materials: a novel application for radiation therapy, Thiago Schmittberger, Giovana Ribeiro Ferreira, Fabrício Aparecido dos Santos, Andrea Gomes Campos Bianchi, Rodrigo Fernando Bianchi, Universidade Federal de Ouro Preto-Ouro Preto -MG, Marcelo Frota Saraiva, Fundação Cristiano Varella, Hospital do Câncer-Muriaé- MG ■ Conjugated polymers have been appeared as very promising materials for use in next generations of displays, not only because of their good processability in solutions and lightweight, but also due to their higher lumiance with low power consumption. However, even though they are good candidates for lighting applications, they still have major problems in terms of stability. Because of their conjugated nature, they are highly susceptible to degradation processes which dramatically change the emission color and reduce the efficiency and durability of their devices. Apart from the degradation processes due to electrical and/or thermal effects, there is also a need for suitable polymers which are inherently resistant to photoxidation process. This result reveals, on the one hand, the low reliability of polymer devices, and on the other reflects the possibility to design and develop dosimeters where the effects of radiation on the optical properties of conjugated polymers are more important than improving the luminance and lifetime of the light-emitting devices made from them. Moreover, high-energy X ray is desired specially in radiation therapy for cancer treatment where overdose and error in software and operation is not infrequent in literature. In this work we investigated the photoemission from poly(2-methoxy-5(2′-ethylhexylxyloxy)-p-phenylenevinylene) (MEH-PPV) and Tris(8-hydroxyquinolinate)aluminium (Alq3) solutions under the effect of low-dose radiation (6 MeV) delivered by linear accelerators for use in radiation therapy. The results show that the MEH-PPV/Alq3 solution presents a gradation of color from orange to yellow clearly, while its peak position emission shifts from orange-red (571 nm) to green (540 nm) with an estimated radiation dose from 0 to 100 Gy. Finally, the optical response of MEH-PPV/Alq3 system to radia-
tion was investigated to design and develop an electronic device to easily represent the radiation dosage generally used in radiation therapy. The basic idea behind this concept considers the sensor as a traffic light device where red represents underdose and green the prescribed dose or overdose. This work was sponsored by Fapemig, Capes, CNPq and INEO/CNPq.

[11/05/10 - P013] Robust Acene-based Polymer Blends for Flexible Electronics, M. M. Ibrahim, A. C. Maciel, C. P. Watson, A. M.-B. Madec, School of Electronic Engineering, Bangor University, Dean Street, Bangor, Gwynedd LL57 1UT, UK, S. G. Yeates, Organic Materials Innovation Centre, School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK, D. M. Taylor, School of Electronic Engineering, Bangor University, Dean Street, Bangor, Gwynedd LL57 1UT, UK. We report the first measurements demonstrating the stabilisation of semicrystalline organic semiconductor behaviour by blending with an insulating polymer—an important step for improved roll-to-roll printing of organic electronic circuits. In this work, organic thin film transistors (TFTs) were fabricated from 1,4,8,11-tetramethyl-6,13-triethyldisilylethynylpentacene (TMTES-pentacene) either directly or blended with isoactic poly(α-vinyl naphthalene) (iPVN). Measurements made on devices several days after fabrication showed some degradation compared to previous reports: in air, saturation hole mobilities were \( \sim 0.3 \text{ cm}^2/\text{Vs} \) for the pure semiconductor and \( \sim 0.07 \text{ cm}^2/\text{Vs} \) in the blend which, under vacuum, decreased to \(~0.06\) and \(~0.04\) cm\(^2/\)Vs respectively. During further measurements over the temperature range 353 K down to 153 K, the TMTES-pentacene devices either failed completely or displayed significantly reduced mobility upon warming to room temperature. On the other hand, TFTs formed from the blend showed little further degradation although detailed analysis suggests that the saturation mobility is dominated by a parasitic resistance in series with the accumulation channel. The width-normalised resistance is \( \sim 230 \text{ kΩ.cm} \) at room temperature with an activation energy \( \sim 0.07 \text{ eV} \). From subsidiary measurements we conclude that the resistance is associated with the bulk semiconductor between the source-drain contacts and the channel. Reducing this resistance could lead to significantly improved device performance.

+ Permanent Address: National Center for Radiation Research and Technology,
P.O.Box 29, Nasr City, Cairo, Egypt
† Permanent Address: Institute of Physics, USP, São Carlos, Brazil
² email: d.m.taylor@bangor.ac.uk

[11/05/10 - P014] Poly(3-hexylthiophene) Langmuir-Schaefer films for organic electronics, ÉLDER MANTOVANI LOPES, FELIPE GONÇALVES VEIGA, NERI ALVES, FLÁVIO MAKOTO SHIMIZU E JOSÉ ALBERTO GIACOMETTI, Faculdade de Ciências e Tecnologia, UNESP, 19060-900, Presidente Prudente, SP, Brazil. The charge carrier mobility of a semiconductor is the critical parameter that determines the performance of several electronic devices. Poly(3-hexylthiophene) (P3HT) presents one of highest mobility among other organic materials and its value depends significantly on the film preparation processes, thermal treatment and the solvents used for deposition. So, understanding the relationship between these parameters is a fundamental task to improve the organic electronic technology.

Thin polymeric films are usually prepared from spin-coating and casting. Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques, however, allow the fabrication of ultrathin polymeric films, with higher molecular control. Nevertheless, P3HT Langmuir monolayers are quite rigid, which impairs their transfer to a substrate, making difficult the film fabrication. In this work, we show that it is possible to fabricate LS thin films if the P3HT is dissolved in a solvent mixture. The study was accomplished using chloroform (CHCl_3) and tetrahydrofuran (THF) to prepare P3HT solutions. P3HT Langmuir monolayers were characterized by pressure versus area (\(\pi-A\)) isotherms, stability and hysteresis measurements in different experimental conditions. The solvents proportions, the volume and the concentration of the spread solutions were varied. For sake of comparison, monolayers of P3HT dissolved in CHCl_3 hybridized with the liquid crystal 5CB were also studied. The best monolayer was obtained for the solution prepared with 50% of CHCl_3 and 50% of THF, using a P3HT concentration of 0.2 mg/mL and spreading the volume of 300 μL over the subphase. The results showed that, for all solutions, the optimal surface pressure to the monolayer transfer is in the range from 20 to 30 mN/m. The P3HT monolayer prepared with CHCl_3 hybridized with 5CB showed similar results compared to the ones described previously. After the transfer of monolayers to a glass substrate, the resulting LS films were analyzed by UV-Vis spectroscopy and optical microscopy. Results showed that LS films of good quality can be obtained by mixing CHCl_3 with THF. MIS devices using the P3HT LS films were also fabricated. They showed a good electrical characteristic compared to a typical P3HT device. Detailed characterization of the LS films is now under investigation, but the results above described already show that the CHCl_3 and THF solvent mixture open a new possibility to fabricate P3HT Langmuir-Schaefer ultrathin films for organic electronics.

[11/05/10 - P015] Poly(3-hexylthiophene) Langmuir-Schaefer and poly(amideimide) films for using in MIS capacitor devices, ÉLDER MANTOVANI LOPES, RICARDO SUSHUMI YWATA, NERI ALVES, FLÁVIO MAKOTO SHIMIZU E JOSÉ ALBERTO GIACOMETTI, Faculdade de Ciências e Tecnologia, UNESP, 19060-900, Presidente Prudente, SP, Brazil. Usually poly(3-hexylthiophene) (P3HT) thin films for OFETs and MIS devices are prepared from casting and spin-coating using solvents liketoluene, trichlorobenzene, xylene, and chloroform. Also, until now, to the best of our knowledge, there are no reports of the use of thin films fabricated by the Langmuir-Blodgett (LB) or Langmuir-Schaefer (LS) techniques for OFET/MIS devices.
In this work, we will show that it is possible to fabricate MIS devices using as the semiconductor layer P3HT deposited by the LS technique. The P3HT was dissolved using a mixture of the solvents chloroform (CHC13) and tetrahydrofuran (THF) at the same proportion as described in our work to be present in this conference. The MIS device was fabricated as follows. First, the insulating layer of poly(amideimide) (PAI) was spin-coated on the top of a slide ITO glass. This polymeric layer was cured at 150°C for one hour and at 250°C for another hour. The LS P3HT thin film was made using about eighty P3HT monolayers and deposited on the top of PAI insulating layer. Finally, a 2 mm diameter silver electrode was deposited by thermal evaporation. The thicknesses of the insulating and semiconducting layers are approximately 300 nm and 200 nm, respectively. It is worth mentioning that the PAI polymer is an insulating material not yet employed in organic electronics. It has the advantage to be easily prepared; it can be thermally crosslinked and exhibits very good insulating properties.

Impedance spectroscopy was used to characterize the PAI/P3HT MIS devices. Through capacitance x frequency curves, the semiconductor and the insulator layers thicknesses were calculated giving the values above mentioned. The doping density Na = 10\(^{22}\) m\(^{-3}\) was obtained by the capacitance x voltage curves using the Mott-Schottky expression. The carrier mobility of 10\(^{-6}\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) was calculated from the Na value and using the Maxwell-Wagner relaxation time, obtained through the maximum of the loss versus frequency curve. Such values are in good agreement with results found in the literature for P3HT typical devices.

In summary, we first report the preparation of P3HT MIS device using the Langmuir-Schafer technique and using the crosslinked poly(amideimide) insulating polymer. We believe that reliable MIS and OFETs devices of the P3HT/PAI could be prepared with a very good performance.

**[11/05/10 - P016]**

**Modeling the response of organic metal-insulator-semiconductor (MIS) capacitors**, F. P. Sabino, N. Alves, J. A. Giacometti, E. M. Lopes, Faculdade de Ciências e Tecnologia, UNESP, 19060-900, Presidente Prudente, SP, Brazil

**Modeling the response of organic metal-insulator-semiconductor (MIS) capacitors**

**MIS capacitors based on P3HT and aluminum oxide**, Donizete Aparecido Buscatti Júnior, Fernando Pereira Sabino, Elder Mantovani Lopes, Neri Alves, Faculdade de Ciências e Tecnologia, UNESP, 19060-900, Presidente Prudente, SP, Brazil

The MIS capacitor is a powerful tool to study the electric properties of the semiconducting and insulating materials and also their interface. On electronic organic, the MIS capacitors have been used to determine the doping density and the mobility of semiconductor, the interfacial states density and others parameters. This device has also a great potential for application in organic sensors, although it is still few explored until now. The poly(3-hexiltionphene) (P3HT) is a semiconductor polymer that is very interesting for use in gas sensors and the aluminum oxide (Al\(_2\)O\(_3\)) has good characteristics for gate insulator. This work shows the characterization of a MIS capacitor made with P3HT and Al\(_2\)O\(_3\) aiming the application as gas sensor. To obtain the Al\(_2\)O\(_3\) film, first a thick aluminum layer was deposited on the top of a glass slide by thermal evaporation in vacuum. Then, an oxide film of about 100 nm thickness was produced by anodisation. The anodisation process is stopped at a certain time so that an aluminum layer remains under the oxide film. This aluminum layer provides the gate electrode for the MIS device. A solution of 2 g/ml of P3HT in chloroform was
casted on the oxide surface, forming a film of about 350 nm thickness. Finally, circular gold electrodes with a diameter of 3 mm were deposited on the P3HT film to complete the MIS device. The complete capacitance and dielectric loss curves, going from the accumulation to the depletion, was obtained between -3V and 3V; because the insulator was very thin and has a high dielectric constant. Measurements were performed with the device in the air, after long exposure to the atmosphere, or annealing at 100 °C for 12 hours. Using Mott-Schottky relation, the doping density \( N_a = 1.2 \times 10^{16} \text{ cm}^{-3} \) was determined for the P3HT from the capacitance versus voltage curve. The mobility \( \mu = 3.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}\text{V}^{-1} \) was calculated using the Maxwell-Wagner peak that appears in the dielectric loss versus frequency curve, measured in the accumulation regime. A series of capacitance and dielectric loss measurements varying the frequency and the voltage applied to the gate will be presented, providing a complete characterization of the MIS device exposed to ambient air. Such characterization is important to evaluate the MIS capacitor as a sensor that must remain exposed to the atmosphere for long time.

**Thermal inkjet printing PANI on paper substrates**

T. C. Gomes, A. E. Job, C. J. L. Constantinno, Neri Alves, Departamento de Física, Química e Biologia, UNESP, Presidente Prudente, São Paulo, Brazil. The polyaniline (PANI) is one of the semiconducting polymers most studied nowadays and very used as active layer in sensors. Its stability at room temperature and its conductivity variation upon some gases exposure (like methanol, benzene and ammonia) makes PANI very attractive from the application point of view. However, its low solubility makes its processability quite difficult. Several techniques are used for thin polymeric films preparation. The inkjet printing technique has been largely explored by the researchers, and it has shown very promising for the preparation of low cost sensors with different architectures. In this work, a commercial thermal printer was used to deposit PANI on common and photographic paper substrates. Powder doped PANI was obtained from the aniline monomer by conventional chemical synthesis. To print PANI using a thermal printer, it is necessary to prepare the PANI "ink" by the following steps: i) dedoping the powder onto an ammonium hydroxide solution; ii) dissolving it in N-Methylpyrrolidone (NMP) (13 mg/ml) and iii) adding ~75%-85% of water. Strips with different gray scales were printed using the Microsoft Word software. Overlapped printings were accomplished at the same substrate position, from one to ten times. Morphological and electrical characterizations were performed as a function of the number of printing, grayscale and substrate type. The morphological analyses, made by optical microscopy, showed that the deposition occurs uniformly. In the DC characterizations, the surface resistivity varied from ~1x10^{-6} \( \Omega^{-1}\square \) to ~10x10^{-6} \( \Omega^{-1}\square \) depending on the number of printing and substrate type. It was observed that the surface conductivity continually grows with the number of printing in photographic paper, while in common paper there is initial growth following by a decrease. The AC characterization, accomplished impedance spectroscopy measurements, evidenced that the films conductivity varies five orders of magnitude when exposed to HCl vapours for doping. Raman measurements showed that there isn't PANI degradation during the ink preparation or the thermal inkjet printing. When comparing the films deposited on common and photographic paper it is observed that the first one shows a smaller variability on the measurements and a larger conductivity dependence on the number of printing and grayscale.

These results show the viability of to print PANI using a thermal printer to produce films with appropriate properties for application in sensors, for example. They also indicate that the use of common paper allows obtaining best electrical and morphological properties.

**Electrical characterization of aluminum oxide thin films fabricated by anodization for metal-insulator-semiconductor devices**

E. C. Ferreira, D. A. Buscatti, Neri Alves, Departamento de Física, Química e Biologia, UNESP, Presidente Prudente, São Paulo, Brazil. The organic electronics is very attractive especially to produce devices covering large and flexible areas, and for low frequency use. Organic field effect transistors (OFETs) based on the MIS structure (metal-insulator-semiconductor) have strategic importance for the development of the organic electronics. However, there are some drawbacks to the commercial use of OFETs, mainly related to the lack of the threshold voltage stability and large operational voltage. The range of the OFET operation voltage is dependent of the threshold voltage, thickness and dielectric constant of the gate insulator. These parameters are more dependent on the gate insulator than on the semiconductor. Consequently, to improve OFETs it is necessary to employ high quality insulators with high dielectric constant, high thermal stability, low leakage current and high breakdown voltage. Furthermore, for organic electronics the insulator material would have the ability to produce very good thin films over large areas, they should be flexible, cheap and easy to obtain. We present the electric characterization of aluminum oxide (\( Al_2O_3 \)) thin films prepared by anodization. Amorphous films of \( Al_2O_3 \) with thickness ranging from 50 to 100 nm and dielectric constant ~9 were produced by oxidation of an aluminum layer deposited onto a glass slide via thermal evaporation. The anodization was accomplished by applying a constant current between the aluminum slide and a gold electrode, both immersed in the aqueous tartaric acid solution (pH = 6). Curves of capacitance, dielectric loss and loss tangent were obtained through impedance measurements in vacuum and in air, after and before thermal treatment and varying the air humidity. In general, \( Al_2O_3 \) thin films present very good insulating properties, with tan\( \delta \) less than 5x10^{-2}. The capacitance as function of frequency after thermal treatment in vacuum is practically constant in the range from 1 Hz to 500 kHz, increasing slightly in low frequencies. It was also
observed that the capacitance and the dielectric loss increase when the air humidity is increased. Morphological analyses with atomic force microscopy (AFM) show that $Al_2O_3$ films are uniform and porous free. In summary, the electrical characterization performed in this work shows that the $Al_2O_3$ presents very attractive properties for fabrication of thin films for application as gate insulator in organic MIS devices.

[11/05/10 - P020] Study of loss curves of MIS capacitors in function of gate voltage, F. P. Sabino, E. M. Lopes, José A. Giacometti, Neri Alves, Faculdade de Ciência e Tecnologia, DFQB - UNESP, Presidente Prudente - São Paulo - Brasil. ■ Organic field effect transistors (OFET) and metal-insulator-semiconductor (MIS) capacitors are very attractive for applications in low frequencies and large areas; also their performance has improved significantly over the past few years. One can employ a MIS capacitor as a powerful tool to characterize the insulator, the semiconductor and the interface insulator-semiconductor properties. For example, the semiconductor doping, mobility and interface states density can be extracted from the dependence of capacitance and dielectric loss on frequency and voltage. In this work, capacitance and dielectric loss curves for organic MIS capacitors are computed through an equivalent circuit. As reference for the calculations a MIS capacitor made from poly(3-hexyliophene) (P3HT) 100 nm thick as semiconductor layer and polysilsesquioxane (PSQ) 200 nm thick as insulator layer. Hence, a doping density of $10^{16}$ cm$^{-3}$ and a resistivity of $10^5$ Ω.m were used. The features observed in the dependence of the dielectric loss on voltage can be explained by considering: i) the parasitic transistor formed by the guard ring and the ohmic contact; ii) the effect of the accumulation layer thickness and iii) the existence of interfacial states, due to traps into the semiconductor band-gap. Each effect generates a peak in the dielectric loss curve. Their characteristics (position and amplitude) are strongly dependent on the frequency. The parasitic transistor effect produces a peak in the accumulation regime which is more pronounced at low and medium frequency range. When the thickness of accumulation layer is considered, the simulation produces a peak in the dielectric loss curve too, which is predominant at intermediate frequency range and the maximum of the peak is always located at flat-band. Interfacial states effects produces a peak in the depletion regime, at low frequencies range, and its amplitude and position depend on interfacial states density and trap capture probability. Therefore, the analysis of the dielectric loss curves versus gate voltage must be carefully done. It is worth to remind that in experimental results, the interfacial states or fixed charges in insulator can change the position of the flat-band. Consequently, if is observed only one peak in the loss curve, it could be erroneously attributed to interfacial states. In summary, this work presents simulations showing how each peak position on the loss curve depends on the frequency, doping density, mobility and other parameters. It is also discussed the conditions where each effect is dominating when the frequency is varied.

[11/05/10 - P021] Langmuir monolayers and Langmuir-Blodgett films of the insulating polymer poly(phenylmethysilesesquioxane): Fabrication and electric characterization, R. S. Ywata, F. M. Shimizu, J. A. Giacometti, Faculdade de Ciências e Tecnologia - UNESP ■ The importance of solvent and subphase pH in the preparation of poly(phenylmethysilesesquioxane), PSQ, Langmuir monolayers were studied using pressure surface vs. mean molecular area isotherms. The goal was determining the best parameters to transfer Langmuir monolayers onto substrates to fabricate high quality insulating Langmuir-Blodgett films for application in organic electronics. Two solvents were used to prepare the PSQ solutions, chloroform which is a usual solvent used to prepare Langmuir and LB films, and butanone often used to prepare PSQ spin coated films. Isotherms of Langmuir monolayers prepared from butanone and chloroform showed extrapolated area values of 53,4 Å$^2$ and 73,5 Å$^2$, respectively, both in aqueous subphase with pH 6. Since both solvents are aprotics, the difference on extrapolated areas could be attributed to different values of molecular weight from solvents (72,11 g/mol for butanone and 119,38 g/mol for chloroform). The subphase pH were varied from 2 to 11 using HCl and NaOH. Results for butanone showed which extrapolated areas are practically independent of pH, but for chloroform was observed a shift from 61,5 to 83,0 Å$^2$ increasing the pH. Monolayer stability measurements at constant surface pressure of 25 mN/m were carried out and an area loss of circa of 10 % for monolayers prepared with chloroform and ~14 % for butanone and they are independent of pH values. Compression and decompression measurements of monolayers were performed up to a surface pressure of 25 mN/m showing a shift of ~8 Å$^2$ on the curve indicating formation of aggregates. It was found that best conditions for the transference of monolayers to a quartz substrate were obtained for the monolayers prepared with chloroform and subphase with pH 3. UV-Vis spectroscopy showed a linear profile for the plot of maximum absorbance at 190 nm versus the number of transferred monolayers, indicating a LB film with good quality. Impedance spectroscopy measurements were performed using 70-monolayers LB and spin-coated PSQ films prepared with butanone and chloroform. Superficial treatments with hexamethyldisilazane were done on both films. LB film shows capacitance of ~255 µF/cm$^2$, while spin-coated films showed capacitance value of ~80 µF/cm$^2$. Tanδ presents values relatively high for all films, ranging from 10$^{-2}$ to 10$^2$, showing that electrical properties of LB PSQ film appears to be relatively better than spin-coated films.