

Personal Information



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Studies

- 2002-2006 PhD Degree: "Nanostructures and Interfaces of Organic and Inorganic Materials and Processes", Aristotle University of Thessaloniki (Scholarship)
- 1999-2002 MSc Degree: "Study of Thermoelectric Materials", Aristotle University of Thessaloniki (Scholarship)
- 1994-1999 Physics Degree, University of Crete

Work Experience

- **June 2007-August 2014:** Post-Doctoral Researcher [Nanotechnology Lab LTFN](#) of Aristotle University of Thessaloniki [Physics Department](#)
 - Activities
 - Materials Characterization by X-Rays
 - Thin Films deposition by Physical Vapor Deposition and Wet Methods
 - Ion Surface Treatment
 - R&D Projects Submission & Implementation
- **September 2014-Today:** Special Laboratory Teaching Staff in Aristotle University of Thessaloniki [Physics Department](#)
 - Teaching
 1. Lab of Applied Informatics (Winter Semester)
 2. Lab of Material Structure (Spring Semester)
 3. Post-Graduate Level Thin Films & Surface Treatment Technology (Winter Semester)

Participation in R&D Projects

National Projects

1. SINERGASIES Project (2011) "Development of Integrated Flexible Textile & Electronic Products (Yfatronic)"
2. SINERGASIES Project (2011) "Development of Nanostructured Organic & Inorganic Materials and Thin Films for the Production of Organic Electronic Devices (NanOrganic)"
3. Pythagoras II (2005-2007) Growth of Carbon and Boron Nitride Nanostructures and Nanotubes and study of their Biocompatibility
4. SYNERGASIA 2011 GR-Light - Green/k Sustainable Lighting
5. NSRF 2014-2020 project (2018-2021) "Semitransparent Organic and Printed Photovoltaics for Energy Efficient Mediterranean Greenhouses"

European Projects

1. "Transparent Films Vacuum Coatings Machine with Integrated In-line Monitoring and Control (TransMach)" GROWTH, Proj. No. GRD1-2000-25437 (2/2001- 12/2003),
2. PolyNET - Network of Excellence for the exploitation of organic and large area electronics "NoE-PolyNET" FP7 Network of Excellence (01/2008 – 12/2010),

3. FlexNet- Network of Excellence for building up Knowledge for improved Systems integration for Flexible Organic and Large Area Electronics (FOLAE) and its exploitation 65574/01-12-2009 FP7 Network of Excellence (01/01/2010 - 31/12/2012) (<http://www.noe-flexnet.eu>)
4. "Development and integration of processes & technologies for the production of Organic Low-cost & large-Area flexible Electronics" (OLATronics) FP7 STREP, (01/2008 – 12/2010), (<http://www.olatronics.org>)
5. COLAE- Commercialization Clusters of OLAE FP7-CSA (01/09/2011 - 31/08/2014) (<http://www.colae.eu>)
6. "Reinforce organic electronics research potential in Kentriki Makedonia" (RoleMak) FP7-REGPOT-2011-1/ 286022 (09/2011 – 08/2014), (<http://www.rolemak.eu>)
7. Development of smart machines, tools and processes for the precision synthesis of nanomaterials with tailored properties for Organic Electronics (SMARTONICS) FP7-NMP, 310229 (01/2013 – 12/2016), (<http://www.smartonics.eu>)
8. Bringing Innovation by Scaling up nanomaterials and inks for printing (BASMATI), H2020-NMP- (2015-2018)
9. Development and implementation of Grouping and Safe-by-Design approaches within regulatory frameworks (NANOREG II), H2020-NMP-2014, (2015-2018)
10. "SMARTLINE - Smart in-line metrology and control for boosting the yield and quality of high-volume manufacturing of Organic Electronics", H2020 - FOF - 08 -2017, (2017-2020)

Publications (Latest)

Articles: 30

Citations 574 (December 2019)

h-index: 10 (December 2019)

[Scopus Profile](#)

Journal Articles

- (A1) Efthimiopoulos T., Dogas D., Palli I., Gravalidis C., Campbell M.
Plasma shielding of a XeCl-laser-irradiated YBCO target
[Applied Physics A: Materials Science and Processing 71 \(2000\) 325-329](#)
Plasma shielding during the laser ablation process of YBCO high-Tc superconductor is demonstrated by observing the transmissivity of a probe beam. A plasma electron density of $1.2 \times 10^{22} \text{ cm}^{-3}$ at the end of the laser pulse is estimated.
- (A2) Efthimiopoulos T., Dogas D., Palli I., Gravalidis Ch., Campbell M.
Screening effects of the excimer laser produced plasma of YBa₂Cu₃O₇
[Journal of Materials Processing Technology 108 \(2001\) 197-200](#)
The radiation screening properties of the excimer laser produced plasma of the YBCO high Tc superconductor were investigated. The plasma was created as a result of the ablation of bulk YBCO in air, following the absorption of 30 ns duration excimer laser pulses and probed by laser pulses of the same characteristics. Plasma shielding was observed above approximately 1.4 J/cm² of laser energy flux. The electron density of the plasma as a function of the laser energy flux, at the beginning of the plasma expansion, was estimated.
- (A3) Patsalas P., Gravalidis C., Logothetidis S.
Surface kinetics and subplantation phenomena affecting the texture, morphology, stress, and growth evolution of titanium nitride films
[Journal of Applied Physics 96 \(2004\) 6234-6235](#)
We present a thorough study of the microstructure, texture, intrinsic stress, surface, and interface morphology of transition metal nitride (mainly TiN but also CrN) films grown on Si by reactive sputter deposition, with emphasis to the mechanisms of adatom migration on the surface and subplantation of energetic species. In order to study the effects of adatom mobility and the subplantation probability we vary the ion energy and growth temperature. For the experimental part of this work we used nondestructive, statistically reliable x-ray techniques (diffraction, reflectivity, scattering). The x-ray results are compared and correlated with supporting data of in situ spectroscopic ellipsometry as well as Monte Carlo simulations of the irradiation effects and surface diffusion of adatoms. We found that the texture and the surface and interface morphology are sensitive to the mechanism of dissipation of the impinging ions. If the energy is enough to overcome the

subplantation threshold (~ 50 eV), then the films are highly compressed and exhibit ultrasoft surfaces and rough interfaces. In this case, the texture of the films is not affected much by the ion energy, since the energy is dissipated in the bulk and contributes less to the surface mobility of adatoms. On the other hand, when the ion energy is below the subplantation threshold the texture of the films strongly depends on the ion energy and flux, the interfaces are atomically sharp and the surface morphology depends on the mobility and surface diffusion length of adatoms. However, in both cases these effects are dominant at the homogeneous growth. At the initial stages of nucleation and island growth the differences in the growth due to irradiation conditions are not pronounced and the thermodynamics of wetting of TiN on Si are prevailing factors.

- (A4) Charitidis C., Laskarakis A., Kassavetis S., Gravalidis C., Logothetidis S.

Optical and nanomechanical study of anti-scratch layers on polycarbonate lenses

[Superlattices and Microstructures 36 \(2004\) 171-179](#)

In recent years, as the optical-electronic industry developed, polymeric materials were gradually increasing in importance. Polycarbonate (PC) is a good candidate for eyewear applications due to its low weight and transparency. In the case of PC lenses, the deposition of anti-scratch (AS) coatings on the polymer surface is essential for the improvement of the mechanical behavior of the lens. In this work, we present a detailed investigation of the optical and nanomechanical properties of a PC based optical lens and coated by an AS coating as a protective overcoat. The study of the effect of the AS coating on the optical response of the PC lens has been performed by the use of Spectroscopic Ellipsometry (SE) in the IR spectral region, where the characteristic features corresponding to the different bonding configuration of the PC lens and the AS coating were studied. Also, the nanomechanical study of the PC lens, before and after the deposition of the AS coating, performed by nanoindentation measurements revealed the significant enhancement of the mechanical response of the AS/PC lens. More specifically, the AS/PC lens is characterized by enhanced values of hardness and elastic modulus. Finally, the use of AS coating has found to lead to a better scratch resistance and to the reduction of the coefficient of friction (μ) of the PC lens.

- (A5) Gravalidis C., Gioti M., Laskarakis A., Logothetidis S.

Real-time monitoring of silicon oxide deposition processes

[Surface and Coatings Technology 180-181 \(2004\) 655-658](#)

Multi-wavelength ellipsometry in Vis-far UV energy range has been applied for the study and the monitoring of the stoichiometry (x) and optical properties of SiO_x films, grown on c-Si substrates by electron-beam evaporation technique, using different source materials (SiO₂, SiO or SiO_x). The ellipsometric data collected in real-time correspond to 32 different wavelengths covering the range from 1.5 up to 6.5 eV, and are fitted by applying the Tauc-Lorentz model. The calculated optical parameters, such as Penn Gap ω_0 and the fundamental band gap ω_g , are directly correlated to x values. In addition, the close monitoring of the deposition processes provides the ability to study the growth mechanisms that are discussed in terms of the source material and the predominant precursors during deposition. Therefore, this methodology reveals the potential for real-time control of SiO_x films' growth of desirable stoichiometry or a functionally graded one, meeting specific demands for microelectronics or other industrial applications.

- (A6) Gravalidis C., Logothetidis S., Hatziaras N., Laskarakis A., Tsiaoussis I., Frangis N.

Characterization of Si nanocrystals into SiO₂ matrix

[Applied Surface Science 253 \(2006\) 385-388](#)

Silicon nanocrystals (nc-Si) have gained great interest due to their excellent optical and electronic properties and their applications in optoelectronics. The aim of this work is the study of growth mechanism of nc-Si into a-SiO₂ matrix from SiO/SiO₂ multilayer annealing, using non-destructive and destructive techniques. The multilayer were grown by e-beam evaporation from SiO and SiO₂ materials and annealing at temperatures up to 1100 °C in N₂ atmosphere. X-rays reflectivity (XRR) and high resolution transmission electron microscopy (HRTEM) were used for the structural characterization and spectroscopic ellipsometry in IR (FTIRSE) energy region for the study of the bonding structure. The ellipsometric results gave a clear evidence of the formation of an a-SiO₂ matrix after the annealing process. The XRR data showed that the density is being increased in the range from 25 to 1100 °C. Finally, the HRTEM characterization proved the formation of nc-Si. Using the above results, we describe the growth mechanism of nc-Si into SiO₂ matrix under N₂ atmosphere.

- (A7) Logothetidis S., Laskarakis A., Kassavetis S., Lousinian S., Gravalidis C., Kiriakidis G.

Optical and structural properties of ZnO for transparent electronics

[Thin Solid Films 516 \(2008\) 1345-1349](#)

During the last years there has been an enormous research effort on the materials and processes for the production of transparent electronic devices grown on flexible polymeric substrates as well as on rigid substrates, such as Si and glass. The deposition of Transparent Conductive Oxides (TCOs) characterized by superior optical and electrical properties, in combination to desirable growth characteristics, compatible to polymeric substrates, is of considerable importance. Among all TCO materials, Zinc Oxide (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties, its high chemical and mechanical stability and, due to its abundance, low cost compared with the most currently used TCO materials. In this work, we study the effect of the deposition parameters of ZnO thin films in terms of their optical, structural and nanomechanical properties by employing Spectroscopic Ellipsometry (SE) in the Vis-fUV spectral region, and X-Ray Diffraction techniques. The SE measurements allowed the determination of the optical properties of the ZnO thin films with deposition time and gas partial pressure, whereas the XRD measurements revealed that the ZnO thin films are preferentially grown parallel to (002) axis, in grains less than 10 nm. Furthermore, nanomechanical testing through nanoindentation indicates a thickness controlled fracture mechanism (pop-in events) affecting the durability of the deposited ZnO thin films.

- (A8) Gravalidis C., Laskarakis A., Logothetidis S.

Fine tuning of PEDOT electronic properties using solvents

[EPJ Applied Physics 46 \(2009\) 12505p1-12505p4](#)

Non-destructive method of spectroscopic ellipsometry (SE) from IR to FUV was applied to study PEDOT/PSS thin films deposited by spin coating from aqueous dispersions of the material with different N,N-Dimethylformamide (DMF) volume percent. In our work we used the Tauc-Lorentz model to describe the dielectric function of PEDOT/PSS:DMF films in the Vis-FUV energy region. First, the spectrum analysis showed that the thickness and the fundamental band gap of the film is being decreased with the increase of DMF content in the dispersion. Taking into account that the heating temperature is below the boiling point of DMF we assume that DMF molecules are incorporated in the film volume and act as dopants. Further more, this means that carrier concentration is being increased and thus we have higher electrical conductivity. The existence of DMF molecules in the film proved from FTIR SE, which can probe the bonding structure of the materials. The results showed lowering of peak intensity assigned to PEDOT/PSS and appearing of peaks assigned to DMF in the imaginary part of spectrum. In conclusion, SE is a potential tool for the evaluation of electronic properties for conductive polymers.

- (A9) Laskarakis A., Kassavetis S., Gravalidis C., Logothetidis S.

In situ and real-time optical investigation of nitrogen plasma treatment of polycarbonate

[Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 268 \(2010\) 460-465](#)

Polycarbonates are very attractive polymeric materials with extensive applications in optical technology as well as for replacing conventional rigid substrates, such as glass. The use of plasma treatments has been successfully employed for improving their surface properties and increasing adhesion of subsequent functional coatings. The objective of this study is to employ in situ and real-time Fourier transform infrared spectroscopic ellipsometry for a detailed investigation of the effect of nitrogen plasma treatment using a pulsed DC voltage, on the optical properties of polycarbonates. Measurements taken before, during and after plasma treatment showed the formation of a surface overlayer in which macromolecular chain scission takes place. The evolution of the overlayer thickness and its bonding has been investigated in detail. Also, the study of the surface nanotopography of polycarbonates by atomic force microscopy showed that plasma treatment increases the surface roughness.

- (A10) Papadopoulos G., Anetakis C., Gravalidis C., Kassavetis S., Vouroutzis N., Frangis N., Logothetidis S.

Simple method for coating Si (1 0 0) surfaces with ferritin monolayers - Iron oxide quantum dots

[Materials Science and Engineering B: Solid-State Materials for Advanced Technology 176 \(2011\) 500-503](#)

With the goal to develop iron oxide quantum dots we developed a simple method to spread horse spleen

ferritin monolayers on a Si (1 0 0) surface. Application of atomic force microscopy and spectroscopic ellipsometry showed the existence of regions with dense ferritin monolayers. Application of transmission electron microscopy identified the core of the spread ferritin as FeO nanocrystals.

- (A11) Tsydel I., Kucinska M., Marszalek T., Rybakiewicz R., Nosal A., Jung J., Gazicki-Lipman M., Pitsalidis C., Gravalidis C., Logothetidis S., Zagorska M., Ulanski J.

High-mobility and low turn-on voltage n-channel OTFTs based on a solution-processable derivative of naphthalene bisimide

[Advanced Functional Materials 22 \(2012\) 3840-3844](#)

In organic electronics solution-processable n-channel field-effect transistors (FETs) matching the parameters of the best p-channel FETs are needed. Progress toward the fabrication of such devices is strongly impeded by a limited number of suitable organic semiconductors as well as by the lack of processing techniques that enable strict control of the supramolecular organization in the deposited layer. Here, the use of N,N'-bis(4-n-butylphenyl)-1,4,5,8-naphthalenetetracarboxylic-1,4:5,8-bisimide (NBI-4-n-BuPh) for fabrication of n-channel FETs is described. The unidirectionally oriented crystalline layers of NBI-4-n-BuPh are obtained by the zone-casting method under ambient conditions. Due to the bottom-contact, top-gate configuration used, the gate dielectric, Parylene C, also acts as a protective layer. This, together with a sufficiently low LUMO level of NBI-4-n-BuPh allows the fabrication and operation of these novel n-channel transistors under ambient conditions. The high order of the NBI-4-n-BuPh molecules in the zone-cast layer and high purity of the gate dielectric yield good performance of the transistors.

- (A12) Kalfagiannis N., Karagiannidis P.G., Pitsalidis C., Panagiotopoulos N.T., Gravalidis C., Kassavetis S., Patsalas P., Logothetidis S.

Plasmonic silver nanoparticles for improved organic solar cells

[Solar Energy Materials and Solar Cells 104 \(2012\) 165-174](#)

In the present work we compare the performance of organic solar cells, based on the bulk heterojunction system of P3HT:PCBM when adequate silver nanoparticles (NPs) are incorporated in two distinct places among the device structure. Introduction of NPs on top of the transparent anode revealed better overall performance with an increased efficiency of 17%. Alternatively, placing the NPs on top of the active photovoltaic layer resulted to 25% higher photo-current generation albeit with inferior electrical characteristics (i.e series and shunt resistance). Our findings suggest that enhanced scattering to non-specular directions from NPs site is maximized when penetrating light meets the particles after the polymer blend, but even this mechanism is not sufficient enough to explain the enhanced short circuit current observed. A second mechanism should be feasible; that is plasmon enhancement which is more efficient in the case where NPs are in direct contact with the polymer blend. J-V characteristics measured in the dark showed that NPs placed on top of the ITO film act as enhanced hole conducting sites, as evident by the lower series resistance values in these cells, suggesting this mechanism as more significant in this case.

- (A13) Kassavetis S., Gravalidis C., Logothetidis S.

Thin film deposition and nanoscale characterisation techniques

[NanoScience and Technology 59 \(2012\) 105-129](#)

In this chapter the basic categories of the thin film deposition techniques are presented. The rf magnetron sputtering (MS) deposition conditions and their effect to the optical, nanostructural and nanomechanical properties of: (a) single layer and multilayer, hard and soft carbon-based thin films grown on rigid Si substrate and (b) AlO_x thin films grown on flexible polyethylene terephthalate (PET) substrate are presented and discussed. Finally the Spin coating technique for the development of thin films from the liquid phase and the solvent effect to the PEDOT:PSS thin film thickness are given.

- (A14) Kapnopoulos C., Mekeridis E.D., Tzounis L., Polyzoidis C., Zachariadis A., Tsimikli S., Gravalidis C., Laskarakis A., Vouroutzis N., Logothetidis S.

Fully gravure printed organic photovoltaic modules: A straightforward process with a high potential for large scale production

[Solar Energy Materials and Solar Cells 144 \(2016\) 724-731](#)

In this work, we describe a novel approach for the fabrication of flexible organic photovoltaic (OPV) modules

with an inverted architecture by a versatile and scalable gravure printing process. The printing has been carried out using a sheet-to-sheet (S2S) lab scale proofer, while all the printing steps were performed in ambient conditions and were optimized for each of the OPV layers. Commercially available zinc oxide (ZnO) ink was used as the electron transport (ETL) layer, poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) blend comprised the bulk heterojunction (BHJ) photoactive layer, poly-3,4-ethylenedioxythiophene:poly(styrenesulfonic-acid) (PEDOT:PSS) was used as the hole transport layer (HTL), and silver (Ag) nanoparticle ink was used as the top contact electrode. The four OPV layers have been successively printed on indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrate using the same printing parameters, allowing the high production throughput in a roll-to-roll (R2R) printing process. The printed OPV modules have size of 45 cm² with an active area of 8 cm² composed of 8 interconnected cells and exhibited a maximum power conversion efficiency (PCE) of 2.22%. The printing parameters were optimized by the contribution from extensive morphological characterization carried out by scanning and transmission electron microscopy (SEM, TEM), as well as from Spectroscopic Ellipsometry (SE) for the determination of the printed layers thickness, optical properties and photoactive layer blend morphology. The above approach revealed the required printing parameters for the further optimization of the layer interface, morphology, thickness and substrate properties in order to implement the above methodology for large-scale manufacturing of flexible OPVs by a R2R process.

(A15) Laskarakis A., Karagkiozaki V., Georgiou D., Gravalidis C., Logothetidis S.

Insights on the optical properties of poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) formulations by optical metrology

[Materials 10 \(2017\) 959 -](#)

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is among the most widely used polymers that are used as printed transparent electrodes for flexible Organic Electronic (OE) devices, such as Organic Photovoltaics (OPVs). The understanding of their optical properties and the correlation of the optical properties with their electronic properties and metallic-like behavior can lead to the optimization of their functionality as transparent electrodes in multilayer OE device architectures. In this work, we study the optical properties of different PEDOT:PSS formulations by non-destructive Spectroscopic Ellipsometry (SE), from the infrared to the far ultraviolet spectral regions. The optical response of PEDOT:PSS includes an intense optical absorption originated from the conductive part (PEDOT) at lower photon energies, whereas the electronic transition energies of the non-conductive PSS part have been measured at higher photon energies. Based on the different PEDOT:PSS formulations, the optical investigation revealed significant information on the relative contribution of conductive PEDOT and insulating PSS parts of the PEDOT:PSS formulation in the overall optical response, which can strongly impact the final device functionality and its optical transparency.

(A16) Kamaraki C., Zachariadis A., Kapnopoulos C., Mekeridis E., Gravalidis C., Laskarakis A., Logothetidis S.

Efficient flexible printed perovskite solar cells based on lead acetate precursor

[Solar Energy 176 \(2018\) 406-411](#)

The impressive increase of power conversion efficiency of hybrid perovskites within a few years has made perovskites one of the most promising materials for photovoltaic applications. However, the route to their commercialization necessitates the establishment of reliable and reproducible large-area fabrication of high efficient perovskite-based solar cells. In this paper, we report the fabrication of flexible, printed, lead acetate – based perovskite solar cells under ambient conditions by slot–die coating. The adoption of lead acetate as a precursor ensured the fast crystallization of the perovskite by one–step deposition method, without a further annealing step, suggesting a rapid and low–temperature procedure. The optimization of the processing temperature and the thickness of PCBM layer were proved to be key factors for device performance. The crystal formation of perovskite was confirmed by X-Ray Diffraction and the thickness values of each layer of the inverted device structure were derived by Spectroscopic Ellipsometry. Moreover, Atomic Force Microscopy verified the low value of roughness of perovskite film along with the effective planarization of PC60BM layer. Finally, we report a reproducible, scalable, Roll–to–Roll compatible fabrication process of efficient perovskite solar cells exhibiting performance up to 6.5%.

(A17) Koutsiaki C., Kaimakamis T., Zachariadis A., Papamichail A., Kamaraki C., Fachouri S., Gravalidis C., Laskarakis A., Logothetidis S.

Efficient combination of Roll-to-Roll compatible techniques towards the large area deposition of a polymer dielectric film and the solution-processing of an organic semiconductor for the field-effect transistors fabrication on plastic substrate

[Organic Electronics 73 \(2019\) 231-239](#)

Flexible Organic Field-Effect Transistors (OFETs) constitute nowadays a highly promising field of the organic and printed electronics due to their multiple applications (flexible displays, sensors etc.). However, their cost-effective fabrication by large area Roll-to-Roll compatible printing methods still remains a challenge for their integration to commercial products. In this work, the moderate speed (1 m/min) process of the flexible cross-linked Poly(4-vinyl phenol) (PVP) polymer gate dielectric layer was carried out by integrating a slot-die method that mimics the Roll-to-Roll (R2R) coating conditions, in combination to an airbrush spray method for the solution-processing of the 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-PEN) organic semiconductor. Particularly, the PVP dielectric was slot-die-coated over a 90×15 cm² substrate, while subsequently the TIPS-PEN semiconductor was sprayed onto the 15×20 mm² cPVP-patterned plastic substrates. A surface investigation study on the well-formed slot-die-coated cPVP strips was conducted, revealing desirable dielectric film topography as a result of the good control over the coating process. A detailed analysis of the cPVP thickness evolution along the 90×1.3 cm² patterned stripe, was carried out. The morphological analysis of the sprayed TIPS-PEN layer over the cPVP film revealed well-organized large crystalline domains across the channel area, as a result of the sufficient crystallization time and the excellent cPVP surface morphology. The fabricated bottom gate/top contact flexible OFETs exhibited excellent I-V electrical characteristics with a maximum mobility of 0.21 cm²/V, negligible hysteresis, low threshold voltages (average value of -0.1 V) and on/off current ratios in the range of 103 to $>10^4$. These results demonstrate the potentiality of the proposed scalable methods for the large scale fabrication of high performance low-cost OFET devices.

Peer Reviewed Conference Proceedings Articles

(C1) Logothetidis S., Panayiotatos Y., Gravalidis C., Patsalas P., Zoy A.

X-ray diffuse scattering investigation of thin films

[Materials Science and Engineering B: Solid-State Materials for Advanced Technology 102 \(2003\) 25-29](#)

X-ray Diffuse Scattering (XDS) is presented, a technique, which determines the roughness, morphology and nanoparticle distribution of thin films. XDS is complementary to X-ray Diffraction and Reflectivity (XRD-XRR). The ability of XDS is demonstrated to investigate the films' nanoscale surface structure and to determine additional geometrical features such as correlation length and fractal characteristics. It is shown that XDS can be used for the study of the surface morphology, as well as, phase identification of amorphous materials and combined with XRR for quantitative analysis of composite films using the Distorted Wave Born Approximation (DWBA) with the concept that the film surface behaves like a Self-Affined medium. As model systems we study nanocrystalline Boron Nitride (BN) and amorphous Carbon (a-C) films. XDS spectra of BN films containing both cubic and hexagonal phases exhibit two set of Yoneda peaks, located at angles characteristic of the corresponding BN densities, while BN films containing only hexagonal phase exhibit one characteristic set. This indicates that the two BN phases are not atomically mixed. The opposite: strong atomical mixture of sp² and sp³ components, was found in a-C films by XDS. Additionally, the growth mechanism for a-C films deposited with or without ion bombardment assistance is predicted and discussed.

(C2) Logothetidis S., Gioti M., Gravalidis C.

Optical and electronic characterization on polymeric membranes

[Synthetic Metals 138 \(2003\) 369-374](#)

This work is dedicated to the optical and electronic characterization of poly(ethylene terephthalate) (PET) membranes, which are extensively used in many practical applications. Spectroscopic ellipsometry (SE) from 1.5 to 6.5eV was applied to probe the dielectric function ($\epsilon(\omega)$) of industrially supplied PET membranes and to reveal their optical anisotropy. Two characteristic features were observed at 5.0 and 6.1eV, attributed to electronic transitions occurred in specific chemical bonds of the PET macromolecule. Through the appropriate fitting analysis it was obtained the geometrical structure of the membrane; consisting of a thick amorphous

layer with a crystalline-like layer on top of it, formed during treatment processes. Using Fourier transform infrared (FT-IR) SE it was also extracted the spectral dependence of the $\epsilon(\omega)$ in IR energy range by taking into account the contribution of the PET's vibrational modes, and this it was found to be in an excellent agreement with the SE results.

- (C3) Patsalas P., Logothetidis S., Kennou S., Gravalidis C.

Surface-activation processes and ion-solid interactions during the nucleation and growth of ultra-thin amorphous carbon films

[Thin Solid Films 428 \(2003\) 211-215](#)

Amorphous carbon (a-C) films have been grown by processes using Ar⁺ or C⁺ ions. The films hybridization states were evaluated by Auger electron spectroscopy, X-ray photoelectron spectroscopy and X-ray reflectivity. It was found that the films grown using C⁺ (Ar⁺) exhibit a sp² (sp³) surface, while the deeper monolayers are sp³ (mixed sp³-sp²) bonded. These results were compared with simulations of the ion-solid interactions and the results of a phenomenological model which takes into account the balance between the surface and bulk processes. We found two mechanisms of sp³ formation: on the surface and in the bulk of a-C. We conclude that at medium energy (>100 eV) the surface effects are negligible (for both C⁺ and Ar⁺), while the surface processes dominate when low-energy (~40 eV) Ar⁺ ions are used.

- (C4) Laskarakis A., Gravalidis C., Logothetidis S.

FTIR and Vis-FUV real time spectroscopic ellipsometry studies of polymer surface modifications during ion beam bombardment

[Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms 216 \(2004\) 131-136](#)

The continuously increasing application of polymeric materials in many scientific and technological fields has motivated an extensive use of polymer surface treatments, which modify the physical and chemical properties of polymer surfaces leading to surface activation and promotion of the surface adhesion. Fourier transform IR spectroscopic ellipsometry (FTIRSE) and phase modulated ellipsometry (PME) in the IR and Vis-FUV spectral regions respectively have been employed for in situ and real time monitoring of the structural changes on the polymer surface obtained by Ar⁺ ion bombardment. The polymers were industrially supplied polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) membranes. The Ar⁺ ion bombardment has found to change the chemical bonding of the films and especially the amount of the C=O, C-C and C=C groups. The detailed study of the FTIRSE spectra reveals important information about the effect of the Ar⁺ ion bombardment on each of the above bonding groups. Also, the modification of the characteristic features, attributed to electronic transitions in specific bonds of PET and PEN macromolecules, has been studied using PME.

- (C5) Marszalek T., Kucinska M., Tszedel I., Gravalidis C., Kalfagiannis N., Logothetidis S., Yassar A., Miozzo L., Nosal A., Gazicki-Lipman M., Jung J., Ulanski J.

Transparent and air stable organic field effect transistors with ordered layers of dibenzo[d,d]thieno[3,2-b;4,5-b']dithiophene obtained from solution

[Optical Materials 34 \(2012\) 1660-1663](#)

In a search for solution processable and stable p-type semiconductors an analogue of pentacene namely dibenzo[d,d]thieno[3,2-b;4,5-b']dithiophene (DBTDT) - was tested as an active layer in organic field effect transistors (OFETs). It was found that thin, continuous and transparent films of DBTDT can be obtained with the help of solution based zone-casting technique. This deposition technique allows one to produce highly oriented crystalline layers of DBTDT showing similar molecular arrangement as that of a single crystal. The zone-cast layers of DBTDT were successfully applied in a fabrication process of OFETs with Parylene C[®] used as the gate dielectric. The best parameters are exhibited by the devices with the bottom-gate, top contact configuration: charge carrier mobility of ca 0.02 cm²/Vs and threshold voltage of ca -50 V and performance of these OFETs remains unchanged after 1 months storage in air.

- (C6) Tzounis L., Gravalidis C., Papamichail A., Logothetidis S.

Enhancement of P3HT: PCBM Photovoltaic Shells Efficiency Incorporating Core-shell Au@Ag Plasmonic Nanoparticles

[Materials Today: Proceedings 3 \(2016\) 832-839](#)

We report on a simple and scalable process for the synthesis of core-shell Au@Ag (Gold core @ Ag shell) bimetallic plasmonic nanoparticles (NPs) with an average size in the range of 40 nm, endowing a remarkable improvement of the power conversion efficiency (PCE) of air processed organic photovoltaics (OPVs) upon being deposited onto the active layer. The beauty of the current work lies on the fact that the spin coated OPV devices; exhibiting a normal architecture consisting of a Glass/ITO (Indium Tin Oxide) anode, a poly-3,4-ethylenedioxy-thiophene:poly(styrenesulfonic-acid) (PEDOT:PSS) hole transport layer (HTL), a poly(3-hexylthiophene) (P3HT) and methanofullerene derivative (PCBM) bulk heterojunction (BHJ) photoactive blend layer (P3HT:PCBM), a Au@Ag plasmonic NPs layer, a Calcium (Ca) electron transport layer (ETL), and an Aluminium (Al) cathode, were processed in ambient conditions. The plasmonic NP layer, which was deposited onto the active layer after a short period of O₂ plasma treatment to enhance the adhesion of the water based NP dispersion (limited time of plasma treatment for 20 sec at a pressure of 1.12 mbar and at 10 Watts power), resulted in a 20.1% enhancement of the PCE compared to reference devices. Namely, the PCE was enhanced from 2.24 to 2.69%. The spin coating parameters for the optimum film morphology, thickness, optical properties, etc of all the OPV layers, as well as the desirable morphology at the nanometer scale of the BHJ have been followed according to previous established protocols. Ultraviolet visible (UV-vis) spectroscopy demonstrated the localised surface plasmon resonance (LSPR) peak of the plasmonic NPs. Scanning and transmission electron microscopy (SEM, TEM) depicted the distribution and the surface coverage of Au@Ag NPs above the active layer as well as their geometry and size, respectively. This study shows for the first time the utilization of plasmonic NPs as a means to improve the PCE of air processed OPVs, which is known to get deteriorated by ambient conditions processing.

- (C7) Polyzoidis C.A., Kapnopoulos C., Mekeridis E.D., Tzounis L., Tsimikli S., Gravalidis C., Laskarakis A., Logothetidis S.

Improvement of Inverted OPV Performance by Enhancement of ZnO Layer Properties as an Electron Transfer Layer

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In the present study we focus on the optimization of NP concentration of ZnO used as an ETL for the fabrication of fully printed inverted OPVs by lab-scale Sheet-to-Sheet gravure technique. The inverted OPV architecture consists of the layer sequence: PET/ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag. By diversifying ZnO nanoparticle concentration, we track the optimum concentration for better OPV efficiencies and try to correlate concentration to the electrical characteristics of the OPV and other ETL characteristics such as thickness, surface morphology and roughness, hydrophilicity etc. Further goal of this work is to achieve a cost-efficient scalability of flexible organic photovoltaics (OPVs), the optimization of the ZnO NPs and of the printing processes.

- (C8) Kapnopoulos C., Mekeridis E.D., Tzounis L., Polyzoidis C., Tsimikli S., Gravalidis C., Zachariadis A., Laskarakis A., Logothetidis S.

Gravure Printed Organic Photovoltaic Modules Onto Flexible Substrates Consisting of a P3HT: PCBM Photoactive Blend

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A novel approach for the fabrication of flexible organic photovoltaic (OPV) modules with an inverted architecture by gravure printing process is presented. The printing has been carried out using a sheet-to-sheet (S2S) lab scale proofer, while all the printing steps were performed in ambient conditions and optimized for each of the OPV layers. Commercially available Zinc Oxide (ZnO) ink was used as the electron transport (ETL) layer, poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) blend comprised the bulk heterojunction (BHJ) photoactive layer, poly-3,4-ethylenedioxy-thiophene:poly(styrenesulfonic-acid) (PEDOT:PSS) was used as the hole transport layer (HTL), and silver (Ag) nanoparticle (NP) ink was used as the top contact electrode. The four OPV layers have been successively printed on indium tin oxide (ITO) coated polyethylene terephthalate (PET) flexible substrate using the same printing parameters. The OPV modules have size of 45 cm² with an active area of 8 cm² composed of 8 interconnected cells and exhibited a maximum power conversion efficiency (PCE) of over 2%. The printing parameters were optimized by the contribution of

extensive morphological characterization by scanning and transmission electron microscopy (SEM, TEM), as well as from Spectroscopic Ellipsometry (SE) for the determination of the printed layers thickness, optical properties and photoactive layer blend morphology. The above approach reveals the required printing parameters for large-scale manufacturing of flexible OPVs by a R2R process.

(C9) Tzounis L., Gravalidis C., Vassiliadou S., Logothetidis S.

Fiber yarns/CNT hierarchical structures as thermoelectric generators

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Due to the increasing demand of alternative energy resources, considerable research interest has been devoted for the development of new thermoelectric materials. Thermoelectric materials are potential candidates for harvesting green energy, due to their ability to generate voltage upon exposure to a temperature difference. Herein, an interesting material used for engineering applications; glass fibers (GFs), were chemically grafted with single- and multi-wall carbon nanotubes (MWCNTs, SWCNTs) and utilized as flexible thermoelectric power generators. CNT-networks were covalently attached onto the surface of intrinsically insulating glass fiber yarns (GF-yarns) following a dip-coating deposition process. The fiber/CNT functional hierarchical yarns showed a maximum power factor (PF) of $\sim 109.8 \mu\text{W}/\text{mK}^2$ (GF-SWCNT). The PF values were found in general to be increased with the increased amount of CNTs grafted onto the fiber surface. The idea of fiber/CNT structures for thermal energy harvesting could be further applied to several consumer applications, such as to smart textiles for wearable applications with the potential of harvesting thermal energy.

(C10) Tzounis L., Stergiopoulos T., Zachariadis A., Gravalidis C., Laskarakis A., Logothetidis S.

Perovskite solar cells from small scale spin coating process towards roll-to-roll printing: Optical and Morphological studies

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Perovskite based solar cells (PSCs) have attracted a huge scientific interest due to their high power conversion efficiencies (PCE) reached already over 20%. However, for solution processed perovskite photovoltaics there are several issues like for i.e. ink concentration, deposition process, temperature, humidity of the environment, etc that have to be addressed in order to obtain devices with high efficiencies and reproducibility of the fabrication process. In addition, it seems that perovskite based photovoltaics will be a very challenging topic for the future, especially for large scale roll-to-roll (R2R) printed PSCs. In this work, a systematic investigation of the morphological and the structural features of perovskite based thin films has been performed. Initially, spin coated devices have been fabricated and characterised (scanning electron microscopy-SEM, X-Ray diffraction-XRD, Photoluminescence-PL) using methylammonium iodide (MAI) mixed with lead acetate (PbAc₂) in dimethylformamide (DMF) as the perovskite precursor ink. The same ink was used also for printing a perovskite layer in ambient atmosphere by slot die coating. Perovskite devices by spin coating have been reached a PCE of 9.4%, while very important has been found to be the thickness of the PCBM layer that from 2000 rpm to 4000 rpm affected the device performance from 4.58% to 9.4%. XRD, SEM and PL have been found to give valuable structural and morphological information, and revealed the optimum experimental parameters for the perovskite absorber formation for high performance operating devices. Printing of Perovskite thin films has been performed with slot die and morphological analysis has been performed to fully realise the perovskite crystallisation process and reveal the optimum conditions for future fully printed PSCs.

(C11) Perli M.D., Karagkiozaki V., Pappa F., Moutsios I., Tzounis L., Zachariadis A., Gravalidis C., Laskarakis A., Logothetidis S.

Synthesis and Characterization of Ag Nanoparticles for Orthopaedic applications

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Bacterial infections are a leading cause of death for millions of people worldwide, while few antibiotics have been proved effective against multidrug-resistant bacteria. Recently, nanoparticles have been used for the delivery of therapeutic agents to reduce bacterial infections due to their antimicrobial activity and unique mode of action. In our studies, silver nanoparticles (Ag NPs) have been used in order to meddle with associated infections for orthopaedic applications, due to their unique morphology and size. Nanoprecipitation method was used for the development of the NPs, using PVP (polyvinylpyrrolidone) as a reducing agent. Chitosan was

used as a stabilizing and a coating agent at different concentrations (0.1%, 0.01% and 0.001%) in order to evaluate the most optimum capped coating. Atomic Force Microscopy (AFM) was the appropriate indicator for the morphological and topography analysis. Results showed that chitosan-capped NPs with 0.01% were found to be the most optimum. Transmittance measurements at plasmon emission at $\sim 320\text{nm}$ wavelength have showed Ag nanoparticles which were identified due to the sharp absorption peak. Variations of the absolute transmittance values due to the different thickness of the samples confirmed the coating of chitosan in Ag NPs. XRD measurements further took place and successfully have indicated the presence of chitosan in Ag nanoparticles' surface. Electrospinning System was used for the formation of PCL (poly- ϵ -caprolactone) scaffolds where Ag NPs were deposited via Electro spraying System. The final scaffolds were then studied with AFM and SEM (Scanning Electron Microscopy) Images. As a conclusion, the fabricated Ag NPs into polymer scaffolds appeared to be a valuable tool with antibacterial properties towards implant-associated orthopedic infections.

(C12) Giannouli M., Karagkiozaki V., Pappa F., Moutsios I., Gravalidis C., Logothetidis S.

Fabrication of quercetin-loaded PLGA nanoparticles via electrohydrodynamic atomization for cardiovascular disease

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Cardiovascular diseases constitute a major public health concern in industrialized nations. Oxidative stress induced free radicals play a critical role in cellular processes implicated in atherosclerosis and many other heart diseases. Quercetin (Qu) is an antioxidant drug which is shown that effectively protects against cardiovascular diseases (CVDs). Encapsulation of drugs in polymeric NPs are widely used in producing sustained and controllable drug release, or to avoid degradation of non-released drugs. In this current work, a novel system of polymeric PLGA NPs loaded with Qu, was fabricated via electrohydrodynamic atomization process (EHDA) in order to improve poor aqueous solubility and stability of the drug with the aim of preventing atherosclerosis. The fabricated nanoparticles collected in a stable glass substrate. The results of atomic force microscopy (AFM) analysis and the scanning electron microscope (SEM), confirmed the fabrication of spherical polymeric nanoparticles with diameter ranging from 300nm to 350 nm, narrow size distribution and smooth surface. The release profile of quercetin from the particles was investigated by determining the drug amount released at specific intervals for by luminescence. Furthermore, XRD analysis was used to determine the physical status of Qu encapsulated in NPs compared with that of pure Qu. The information obtained from this study facilitates the design and fabrication of polymeric nanoparticles as possible delivery systems for encapsulation, protection and controlled release of the flavonoid quercetin which is aiming to protect against CVDs.

Review

(R1) Gravalidis C., Logothetidis S.

X-Ray diffuse scattering investigation of polytetrafluorethylene surfaces
Polimery/Polymers 51 (2006) 359-364

We present the X-Ray Diffuse Scattering (XDS) technique which can determine except for the surface roughness, the distribution of in-plane fluctuations and fractal dimension on the surface. The scattering intensity is calculated using Distorted-Wave Born Approximation (DWBA) and depends on the quantities related both to 1st and 2nd order surface statistics like, surface roughness σ , lateral correlation length ξ and "Hurst coefficient" or "roughness exponent" h ($0 < h < 1$). The samples were prepared by spraying a PTFE dispersion directly on preheated Si wafer, at three different spraying times, following by an annealing process. The aim of this work is to study the effect of spray duration on the surface morphology. Firstly, the amorphization induced due to the annealing was observed by X-ray diffraction measurements. The analysis of the XDS rocking scans gave that the mass density is increased with the spraying time and the roughness is almost the same. However, the surface morphology described also by the distribution of the vertical fluctuations, through the correlation length ξ , showed that the narrow distribution was realized at middle, while broad one at long or short spraying times. Furthermore, the surface exponent h , calculated by XDS off-specular scan, is constant and low, meaning that the low smoothness of the surface is not affected by the spraying time.