Form 1

2017 Report Form for Collaboration with Research Center for Biomedical Engineering

Year/month/date	
Number	2024

13 /3/2018

date:

To Chairman, Board of Directors, Research Center for Biomedical Engineering

Applicant
Affiliation Moldova State University
Title Dr. Assoc. Profesor
Name Tamara Potlog
Address Chisinau, MD 2009 Moldova

Phone 373 69953854
Fax 373 22 244248
E-mail tpotlog@gmail.com

Report Form for Collaboration Research

Research Theme	Development of metal-phthalocyanine-perylene diimide derivates composite materials for photodynamic terapy and photon harvesting in bulk heterojunction photovoltaic devices
Research Area	1. Biomaterials 2. Bioengineering 3. Functional molecules 4. Chemistry/Electrical Engineering/Mechanical Engineering/Materials Science
Research Period	From: Date/month/Year To: Date/month/Year 15/09/2017 - 12/12/2017

Applicant Organization			
Name	Department	Title	Role
Tamara Potlog	Department of Physics and Engineering	Assoc. Prof.	Experiments and analysis
Collaboration Partners in the Research Center	Professor Hidenori Mimura RIE, Shizuoka University		

Research Results (Including Purpose, Results, Figures, etc.)

1. Purpose of Research

The unsubstituted metal phthalocyanines have very low solubility in the majority of the solvents. Therefore, studies focused on investigation of the solubility properties of ZnPc and of photosensitizer composite materials based on ZnPc in different concentrations of solvent. Another objective was fabrication of thin films and annealing at different temperatures, fabrication of the photovoltaic devices based on the developed thin films, characterization and elucidation of the optical, electrical properties in the thin films and devices.

2. Results

Commercially available zinc phthalocyanine (ZnPc) powder (98% purity) was purchased from Sigma Aldrich and was used without further purification. The formic acid (FA) (99% purity) and dimethylformamide (DMF) (99.8% purity) also, purchased from Sigma Aldrich were selected as the solvents for ZnPc. The ZnPc powder was added to the solvents of 60%, 80% and 98% concentrations of formic acid (FA). The X-ray diffractograms of the ZnPc films deposited from FA solution with different concentrations, thicknesses and annealed at 400^{o}C were studied.

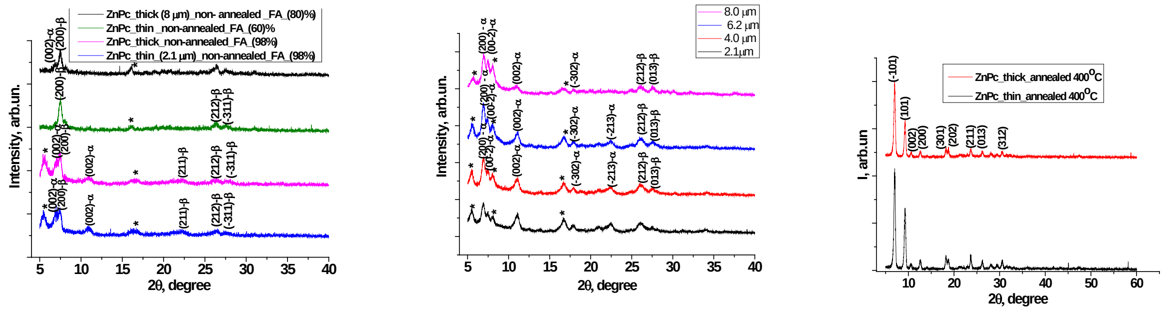

Figure 1 The XRD patterns of ZnPc thin films synthesized on glass substrates from different concentration FA solutions, thickneses and annealed at 400^{o}C.

The XRD results reveal that all as-synthetized ZnPc thin films regardless of the thickness have both α- and β-phases according to the JC-PDS cards No. 21-1986 and 39-1882, respectively. The XRD patterns of ZnPc films annealed at 400 °C are assigned as β-ZnPc phase and are indexed as for monoclinic crystalline structure. FTIR spectra of the non-annealed and annealed at 400^{o}C, of ZnPc thin films were studied. The comparison of them shows that most of the FTIR bands change their position after annealing.

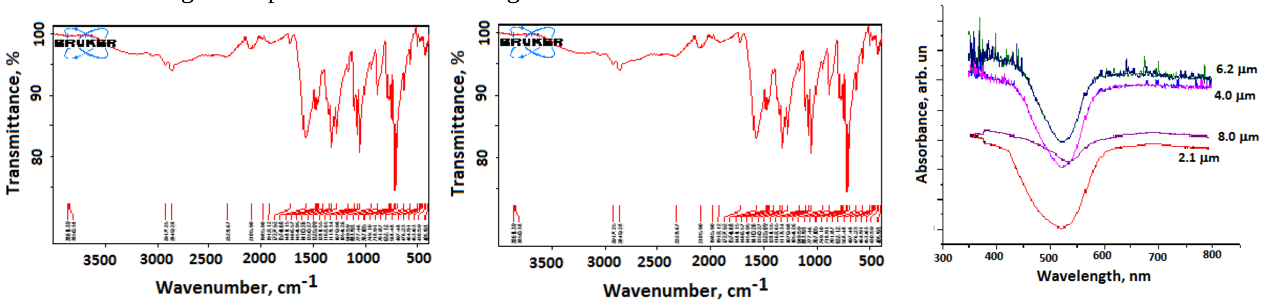

Figure 2 FTIR spectra of 98% FA solution ZnPc thin films of the non-annealed and annealed at 400^{o}C. Absorption spectra of ZnPc (right).

From the absorption spectra the increasing of the absorbance of ZnPc films with further increasing of the thickness are observed. Also, a shift towards the higher wavelength range for the thicker samples is depicted. This shift of spectra indicates the decrease in the optical energy band gap (E_g).

The solution-processable Schottky diode solar cells glass/ITO/PEDOT:PSS/ZnPc(I_2)/Al with different thicknesses of ZnPc layer were fabricated. The J-V characteristics of the device measured at AM1.5 condition (100 mW/cm^2) were measured and photovoltaic parameters were estimated (see table)

The parameter	Vacuum evaporation method [17]	Chemical drop casting method, 8.0 µm and 6.2 µm, respectively	
V_{OC} (V)	0,89	1.03	0.97
J_{SC} ($\mu A \cdot cm^{-2}$)	2,8	8.2	5.6
FF		0.35	0.23
η, %		0.3	0.125

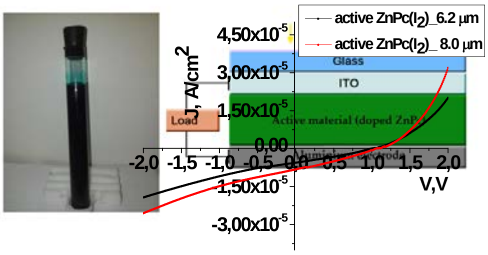

Figure 3 The schematic configuration of solution processable glass/ITO/PEDOT: PSS/ZnPc(I_2)/Al photovoltaic device (left) and the J-V characteristics of solution processable glass/ITO/PEDOT: PSS/ZnPc (I_2)/Al photovoltaic device (right).

ZnPc thin films of various thicknesses, ranging from 2.1 µm to 8.0 µm have been prepared from FA solutions of different concentration using the drop casting method. The XRD and FTIR analysis reveal the formation of Zn(HCOOH)Pc formate supramolecular complexes. Also, XRD analysis shows that the as deposited ZnPc films are polycrystalline and contain a mixture of two crystalline phases: α- and β-. After annealing the improvement of the films crystallinity shown by XRD analysis results in the increasing of the crystallites size from 20 nm to 32 nm and the presence of the only β- phase. Further on, in this paper we demonstrate the fabrication of Schottky diode solar cells with highest open circuit voltage on the base of optimized technology of ZnPc thin films. Moreover, ITO/PEDOT: PSS/ZnPc(I_2)/Al photovoltaic devices have higher efficiency than the devices obtained with thermal vacuum evaporation method. Recently, ZnPc has drawn considerable attention because of employing as hole-transporting material in mixed-ion $[FAP_bI_3]_{0.85}[MAP_bB_{r3}]_{0.15}$ perovskite solar cells, that reaching the highest power conversion efficiency (PCE), 17.5% so far for phthalocyanines. In order to improve the efficiency of solar cells with elaborated ZnPc technology we need to develop the technology of an acceptor. Literature study show that we need to develop technology of a new perovskite.

List of Publications Related to the Collaboration Research

1.T. Potlog, Vadim Furtuna, Cornel Rotaru, Roman Rusnac, Stefan Robu, Hidenori Mimura. Material Properties of Zinc Phthalocyanine from FA Solution and Application in Organic Solar Cells “Proceedings of 38th International Conference”, Tokyo, Japan, Nov. 2017, pp.39-45, ISBN 978-93-87405-42-4.

2. T. Potlog, E. Dauksta, A. Medvids, L. Ghimpu, C. Moise, K. Murakami, H. Mimura. “Effect of Laser Irradiation on the Refractive Index of the TiO_2 Thin Films. Optics and Laser Technology Journal, in press, under review, 2018

List of Presentations (Conference, Meeting, etc)

1. “Structural Properties of Nanostructured Laser Annealed TiO_2 Thin Films” The **34th** International Japan-Korea Seminar on Ceramics, Hamamatsu, November, 2017 (oral presentation)

2. “Material Properties of Zinc Phthalocyanine from FA Solution and Application in Organic Solar Cells” 38th Research World International Conference”, Tokyo, November, 2017

List of Awards

Research plan for the next year (from April 1, 2018 to March 31, 2019), if the collaboration research is continued. Prior consent from the collaboration partner in the Research Center is necessary.
In the next year (2018) will be continued investigation of this materials for application in the photodynamic therapy. **Photodynamic therapy investigations** **Objectives of the research activities will be:** **Firstly,** evidence for the synthesis of **metal-phthalocyanine-polymer photosensitizer composite material will be provided by** XRD, Raman spectroscopy, FTIR spectroscopy and by UV-VIS spectroscopy for identifying the differences determined by using various perylenediimide (PDI) derivatives concentrations and for identifying the specific absorption bands, respectively. **Secondly**, the main research will refer to the assessment of two main parameters featuring the phenomenon of photosensitization: **the quantum yield of the singlet oxygen generation and the singlet oxygen population lifetime.** The singlet oxygen quantum yield is a quantitative measurement of the efficiency in which photosensitizes are able to use energy, in the form of light, to convert oxygen in the ground state to the reactive species singlet oxygen. Singlet oxygen quantum yields of photosensitizes differ when measured in different solvents**. Therefore, lifetime of singlet oxygen as a function of solvent will be thirdly specific objective**. Because of the different physical or chemical aspects of the production of the oxygen molecule in its singlet state, for singlet oxygen detection, different methods, such as fluorescence imaging and fluorescence lifetime imaging microscopy (FLIM), fluorescence lifetime/transient absorption analysis systems (NIR photoluminescence lifetime spectrometer, picoseconds fluorescence lifetime measurement...) and others designed by Hamamatsu Photonics for measuring photoluminescence (PL) spectrum and PL lifetime in the NIR region will be used, if will be available in RIE, Shizuoka University. The choice of light source will depend on the type of photosensitizers. Since PDT is typically constrained to the "use of visible or near infrared light" consisting of localized delivery to tumors, as sources will be lasers, incandescent light sources, light-emitting diodes coupled with optical fibers. Will be choose a longer wavelength of light because increases the penetration depth into the tissue.