

COMPARATIVE SPECTROSCOPIC ANALYSIS OF THIN FILMS AND TARGETS FROM NLO MATERIALS DEPOSITED BY PULSED LASER DEPOSITION

P. Penchev¹, R. Bakalska¹, S. Sotirov², M. Todorova¹, V. Serbezov²

¹University of Plovdiv, Chemical Faculty, 24 Tsar Assen St., 4000 Plovdiv,

*²University of Plovdiv, Dept. of Experimental Physics, Faculty of Physics
office@biocoats.com*

ABSTRACT

Organic dyes such as styrylquinolinium salts are new promising materials for photonic applications. Comparative FTIR spectroscopic analysis on thin films and targets from three new organic compounds, *i. e.* E-4-(2-(4-hydroxynaphthalen-1-yl)-vinyl)-1-octylquinolinium iodide (**1**), (E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)-vinyl)quinolinium bromide (**2**), and 4-{(E)-2-[4-(dimethylamino)naphthalen-1-yl]-ethenyl}-1-methylquinolinium iodide (**3**) deposited by means of Pulsed Laser Deposition (PLD) technique using high power UV Nitrogen laser are described. The thin films are deposited on substrates KBr, 316L SS alloy and aluminium foil. The organic materials are synthesized by Knoevenagel condensation. The thickness of the deposited films ranges from 80 to 300 nm as measured by interferometric method. The targets are formed by a moulding press. Characterization of the films and targets by FTIR spectroscopy showed a small difference between the deposited films and the native materials/targets, and their structure and composition depend on technological parameters.

Keywords: FTIR, Organic Non-linear Optic Dyes, Pulsed Laser Deposition

INTRODUCTION

Organic non-linear optical (NLO) materials vary from polymers to molecular crystals to liquid crystals to organometallic compounds and new hybrid organic/inorganic nanocomposites. Organic NLO devices usually are used as bulk or as thin films structures. Thin films of organic NLO dyes are extremely useful for creating of a surface for photonics applications that can be used as fast optical switches, modulators, devices for frequency mixing processes, sensors, integrated optical circuits for telecommunication and medium for optical computing [1,2]. Relatively low-cost preparation of organic NLO dyes, as well as their active optical properties have stimulated researcher for studying and synthesis of new organic NLO dyes. The styryl dyes with quinoline nucleus were applied to various sensitive materials such as sensitizers or desensitizers formerly. With the development of new technologies the

researchers have found a new application of styrylquinoline dyes to electroluminescence and photochromism [3,4] as well as in the field of medication [5,6].

Classical technologies for deposition these materials as thin films are deep coatings, spin coatings, Langmuir–Blogett method, Molecular Beam Epitaxy and drop-casting technique [7-9]. Advantages and disadvantages are both intrinsic for such of techniques. One disadvantage is the impossibility to deposit thin films with homogeneous and smooth surface without substantial damage of various substrates such as metals, ceramics and organics.

The aim of this work is to study the chemical composition of the surface of the substrates and targets obtained by Pulsed Laser Deposition technique used for preparation of thin films onto KBr, 316L SS alloy and aluminium foil substrates composed by new styrylquinolinium dyes with larger conjugated systems (naphthalene tail with different electron donor group). Comparative FTIR spectroscopic analysis were done for investigation the congruence between chemical structures of thin films and the targets of native material.

EXPERIMENTAL DETAILS

1. NLO organic dyes synthesis

The styrylquinolinium dyes (1) – (3) were synthesized by Knoevenagel condensation of 4-hydroxy- or 4-N,N-dimethylaminonaphtaldehyde and the respective quaternary lepidinium salts in the presence of basic catalyst piperidine. Fig.1 shows the chemical structure of the investigated compounds. The synthesis of merocyanine dyes (1) – (3) was described in ref. [10]. Polycrystalline samples of dyes (1) – (3) suitable for deposition by the PLD technique were obtained after recrystallization from methanol. The synthesized dyes (1) – (3) and their structures and purity were confirmed by ^1H NMR, ^{13}C NMR and UV–Vis spectroscopies, elemental analysis and melting points [10]. The melting points for the target dyes were sharp which indicates a high level of purity and a crystalline phase of the resulting salts.

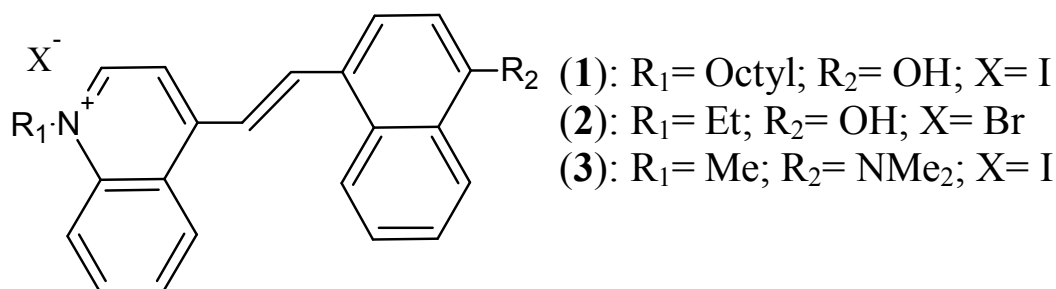


Figure 1. Chemical structure of the investigated compounds.

2. Pulsed Laser Deposition of NLO organic dyes

Experimental setup used for the thin films deposition is typical for PLD technique and is similar with that described beforehand [11]. The organic NLO thin films were deposited in vacuum of 10^{-3} to 10^{-5} Torr produced by a standard rotary pump and diffusion pump. Lambda Physic EMG 102 laser is used as UV TEA N_2

laser with energy per pulse up to 8 mJ, pulse duration 6 ns and repetition rate up to 120 Hz. The angle between focusing laser beam and target is 45° . Short focus of 60 mm meniscus quartz lens were used for focusing laser beam. The distance Substrate–Target (S-T) was varied from 2 cm to 8 cm. The dimensions of substrates for KBr, SS316 L and aluminum foil vary from 2 cm^2 to several dm^2 . The usual distance S-T was 4.5 cm. The target holders is rotated by high speed mini motors mounted inside of vacuum chamber. The single Target is mounted on a regulated high speed motor (up to 3000 rev/s). The Target material consists of one of the styrylquinolinium dyes (1) – (3) for coatings. The Target diameter is 12 mm. The laser beam area at the focus is typically $2 \times 10^{-3}\text{ cm}^2$ to $2 \times 10^{-2}\text{ cm}^2$ and typical laser energy density (so called *fluence*) vary from 3.5 J/cm^2 to 0.35 J/cm^2 . The typical repetition rate of laser pulses is 20 Hz. The rate of coatings' growth at this laser parameters is 0.1 – 0.2 nm/s. The vacuum chamber has been cleaned by means of argon plasma before any deposition process. The experiments were carried out at room temperature.

3. Spectral Measurements

Transmittance and Attenuated Total Reflection (ATR) Fourier Transform Infrared IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR spectrometer (Bruker Optics). The used ATR accessory is MIRacle™ with a one-reflection ZnSe element (Pike). Thin films onto KBr plate were analyzed with absorbance spectra and the depositions onto 316L SS alloy and aluminium foil by ATR spectra.

RESULTS AND DISCUSSION

The spectral analysis of the materials deposited by means of PLD on various substrates is based on comparison of the spectral bands of the obtained thin films with those of the native materials in a region where most of the uncharacteristic fundamental vibrations appear. For this study the $1700 - 600\text{ cm}^{-1}$ spectral interval is selected as it includes the finger print region and the area of the aromatic ring vibration. The spectral analysis will be illustrated with the detail comparison of two spectra of merocyanine dye (1).

The $1700-600\text{ cm}^{-1}$ region of the IR spectrum of dye (1) deposited onto KBr plate is shown in Fig. 2 together with the spectrum of a drop of dye (1) methanol solution dried onto AgCl plate. It can be seen that the two spectral curves look pretty similar and the bands of dye (1) at 1559 cm^{-1} , 1340 cm^{-1} , 1278 cm^{-1} and 957 cm^{-1} are preserved in the spectrum of the thin film. On the other side, some of the bands are shifted up to 10 cm^{-1} which is to be expected as the compound is embedded into the crystal structure of KBr. The strong bands of this type are 1225 cm^{-1} (shifted to 1216 cm^{-1}) and 750 cm^{-1} (shifted to 760 cm^{-1}). The interaction of the deposited dye with the substrate is also a reason for widening of most of the bands. In this case two or three bands close in the compounds spectrum can appear as one (usually unsymmetrical) band in the thin film spectrum. In Fig. 2 these are 1595 cm^{-1} and 1559 cm^{-1} couple, 1363 cm^{-1} and 1340 cm^{-1} couple and 771 cm^{-1} , 761 cm^{-1} and 750 cm^{-1} triad.

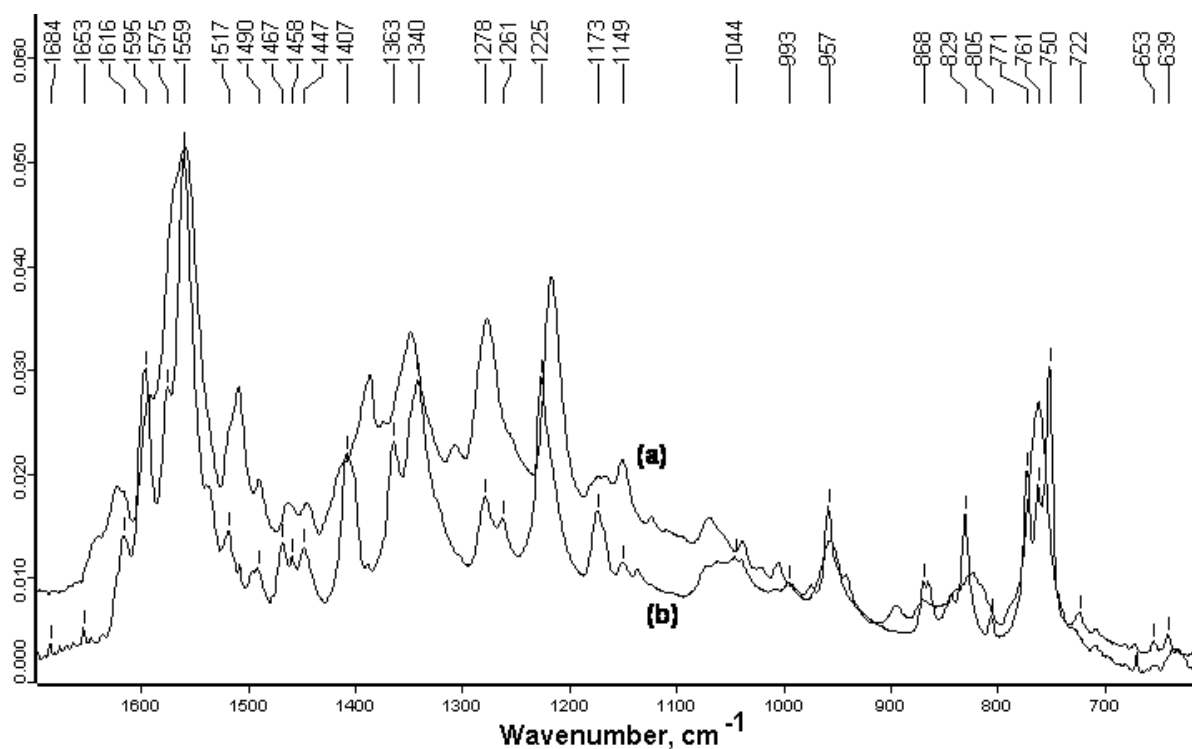


Figure 2. IR Absorbance spectra of dye (**1**); (a) is the spectrum of thin film (the substrate is a KBr plate), and (b) –that of a drop of dye (**1**)’s methanol solution dried onto AgCl plate.

There are two bands in the spectrum of the deposited compound that cannot be explained as a result of deposition – these are the strong 1508 cm^{-1} band and the 1149 cm^{-1} band. The only explanation is that a partial degradation of the deposited compound happens.

As a whole, the high laser fluence (3.5 J/cm^2) used for dye (**1**) deposition had not decomposed heavily the target material. The high fluence shortened the deposition process thus decreasing its cost but it appeared inappropriate for the two other dyes. Thin films of Dye (**2**) and Dye (**3**) deposited on all types of substrates by this high fluence have FTIR spectra which include bands not present in the target compound and which cannot be explained with the peak’s shift discussed above. That is why, the laser fluence was reduced to 0.35 J/cm^2 and the FTIR spectra of the newly obtained thin films were registered and analyzed in a manner described above.

It appeared that the substrate did not influence the quality (expressed mainly as an absence of chemical degradation) of the deposited material and the only factors which determine the dye’s chemical degradation by the deposition process are the laser fluence and the chemical structure of the dye. The relation between dye’s chemical structure and the decomposition rate cannot be comprehended using only our data and is a matter of future studies.

In Table 1 the quality of the deposited materials is given. Usually, several spots in the deposited thin film were measured and it appeared that they had given similar FTIR spectra.

Table 1. *The chemical quality of the obtained thin films of dyes (1) – (3).*

Target	Substrate	Laser fluence [J/cm ²]	Thin film spectroscopic characterization
Dye (1)	KBr 316L SS alloy aluminium foil	3.5	Material is deposited with a little decomposition of dye (1)
Dye (2)	KBr 316L SS alloy aluminium foil KBr	3.5	Material is deposited with a partial decomposition of dye (2)
Dye (2)	316L SS alloy aluminium foil KBr	0.35	Deposited material is virtually not chemically changed
Dye (3)	316L SS alloy aluminium foil	3.5	Material is deposited with a vast decomposition of dye (3)
Dye (3)	KBr 316L SS alloy aluminium foil	0.35	Material is deposited with a little decomposition of dye (3)

CONCLUSIONS

We have successfully demonstrated the application of PLD method using high power TEA N₂ laser ($\lambda = 337.1$ nm) for deposition of thin films of new styrylquinolinium dyes with larger conjugated systems and molecular weight from 300–550 g/mol. The pressed micro crystals targets from complex organic NLO dyes are suitable for PLD process at vacuum in range 10^{-2} mbar to 10^{-3} mbar. Despite the fact, that the higher laser fluence is more costly efficient, it is better to use mild laser fluence in order to avoid target decomposition. As future experiments we need more detailed analysis concerning the UV laser beam interaction with organic target. This first successful study of new laser deposition conditions allow the possibilities for the processing of new class nanocomposites as styrylquinolinium dyes - inorganic nanocoatings with large photonics applications.

Acknowledgements

Authors gratefully acknowledge the financial support by the University of Plovdiv Research Fund (Project RNI 09-HF-002). All experiments of PLD were done with a kind cooperation of MultiCoats Ltd. (<http://www.biocoats.com>).

REFERENCES

1. Chemla, D.S., J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, Ontario, (1987).
2. Trager, F. (Ed.), *Handbook of Lasers and Optics*, Springer Science&Business Media, LLC New York, (2007).
3. Makoto M., T. Hisato, T. Hiromitsu, W. Osamu, M. Tomohiko, T. Seiji, *Jpn Kokai Tokkyo Koho Jpn*, 260, 566 (2000) [Chem. Abstr. (2000), 133, 244894].
4. Spalletti A., *Photochem. Photobiol. Sci.* 3(7), 695-699, (2004).
5. Burdujan R., J. d'Angelo, D. Desmaele, F. Zouhiri, P. Tauc, J.-C. Brochon, C. Auclair, J.-F. Mouscadet, P. Pernot, F. Tfibel, M. Enescu, M.-P. Fontaine-Aupart, *Phys. Chem. Chem. Phys.*, 3, 3797-3804, (2001).
6. Wang, M., M. Gao, K. D. Miller, G. W. Sledge, G. D. Hutchins, Q-H. Zheng, *Eur. J. Med. Chem.* 44, 2300-2306, (2009).
7. Pitt, C. W., *J. Non-Cryst. Solids*, 47, 159-162, (1983).
8. Sanches, C., B. Lebean, F.Chaput, J. P. Boilot, *Adv. Mater.*, 15, 1969-1994, (2003).
9. Quintel, A., F. Budde, P. Rechsteiner, K. Thoma, A. Zayatsb. J. Hulliger, *J. Mater. Chem.*, 10, 27-30, (2000).
10. Bakalska, R., M. Todorova, T. Kolev, Synthesis of new merocyanine dyes as potential NLO materials, 8TH Scientific chemical conference of University of Plovdiv, 18-19 june 2010, Koprivchtitca.
11. Serbezov, V., St. Benacka, D. Hadgiev, P. Atanasov, N. Elektronov, V. Smatko, V. Stribik, N. Vassilev, *J. Appl. Phys.* 67, 6953 -6957, (1990).