

## THERMAL ANALYSIS AND THIN FILMS DEPOSITION BY MATRIX ASSISTED PULSED LASER EVAPORATION OF A 4CN TYPE AZO-MONOETHER

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A new synthesized 4CN type azomonoether, exhibiting dyeing properties, crystalline nature and generating interest as a material for non-linear optical applications was investigated. Modern devices incorporating liquid crystals tend to use thin films of such materials because of their special characteristics. Thermal stability studies are indispensable before attempting any deposition experiment.

We have investigated the thermal behaviour of 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene (TG, DTG, DTA and DSC) in inert flow atmosphere, under non-isothermal conditions. The phase transitions were studied by repeated heating-cooling regimes, with intercalated isothermal steps. The thin films were deposited on silicon and quartz substrates by matrix assisted pulsed laser evaporation (MAPLE) using a Nd:YAG laser working at 266 nm. FTIR spectroscopy of the obtained thin films confirmed the preservation of the compound's structure.

**Keywords:** laser assisted deposition, liquid crystals, MAPLE, phase transitions, thermal analysis, thin film

### Introduction

Liquid crystalline azomonoethers are new synthesized compounds, potential materials for non-linear optical applications. These aromatic azomonoether dyes can be obtained in alkaline medium, by the condensation of 4-(phenylazo)phenols with chloromethylated derivatives of chlorobenzene (the very well known 'Williamson ether synthesis') [1].

Thermal analysis of 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene (4CN type liquid crystal) was performed in order to establish its stability and physical transformations as function of temperature. Recent studies dealing with the thermal behaviour of other azoic dyes were also reported [2–4].

One of the main challenges of materials science is the development and integration of new devices with a wide area of applications. Thermal stability studies are however indispensable before attempting any deposition experiments for obtaining such devices [5–7]. New requirements, as reducing scale dimensions of integrated systems, in our case – thin films, lead to the improvement of new deposition techniques that are producing pure, continuous and smooth surfaces. Laser interaction with matter, since the expansion of pulsed lasers in the mid '60, is the most popular starting point for

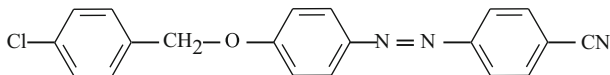
the development of thin films' processing techniques. The most important technique from the technological point of view is pulsed laser deposition (PLD) technique, which was used for the deposition of various uncomplicated inorganic thin films [8, 9]. Laser interaction with matter (solid or liquid materials) implies the obtaining of plasma plume, that transports material, with the formation of a thin film on the substrate. Unfortunately, PLD can not be used as a deposition method as a simple and raw ablation for more complex compounds (organic molecules, inorganic coordination compounds, multi-element oxides, polymers, supermolecules, certain phases, etc.) or systems. This is due to the relatively high laser fluences, that induce photochemical decompositions, and also to the impossibility of transferring such great/complicated structures.

In the last years, a new deposition technique – MAPLE (matrix assisted pulsed laser evaporation), derived from pulsed laser deposition (PLD) concept (thin films' processing by laser interaction type), was set-up to surpass the encountered difficulties [10]. MAPLE technique consists in producing a frozen 'deposition phase-solvent' system and its evaporation when the laser interacts only with the solvent. Such a non-destructive technique seems to solve accurately the deposition problem of complex chemical structures [11–14].

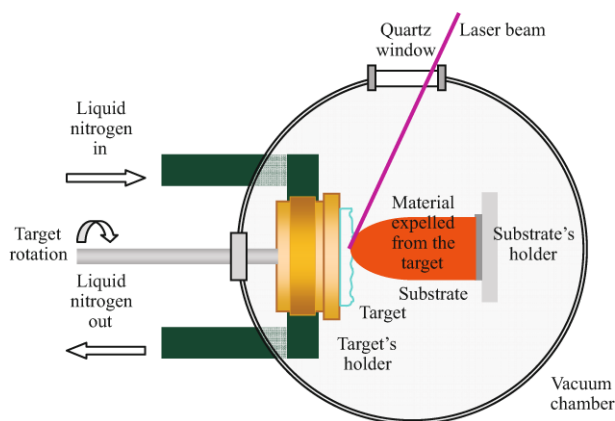
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## Experimental

Azoic dye 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene with liquid crystalline nature,



was deposited on both Si and SiO<sub>2</sub> substrates by MAPLE technique. A Nd:YAG laser, working at a repetition rate of 10 Hz and 266 nm wavelength was used for an incident fluence in the range of 0.066–0.130 J cm<sup>-2</sup>. The experiments were performed for a deposition time of 45 min. The deposition chamber was vacuumed up to 4·10<sup>-3</sup> N m<sup>-2</sup>. The experimental setup of the MAPLE method is presented in Fig. 1.

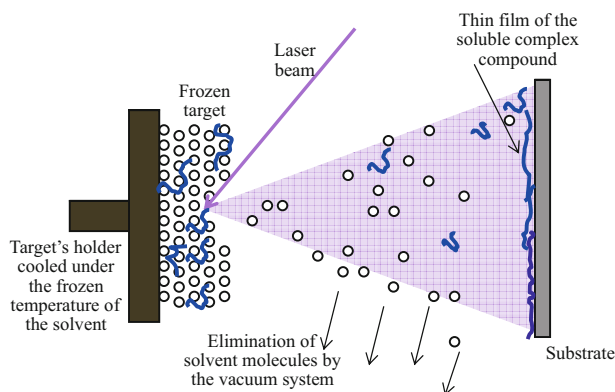


**Fig. 1** Experimental setup of MAPLE deposition technique for thin films fabrication

The targets were prepared by freezing a solution of 0.5% of 4CN type liquid crystal in toluene. Usually, the solution must be of 0.1–2.0 mass% because of the hard laser interaction with the solid target; the chosen solvent is preferable to have a freezing point as high as possible.

When the laser reaches the target, only the solvent (also named – matrix) is absorbing the radiation. Thus, the ‘solid’ is ablated, the matrix evaporates and only the material’s molecules are collected on the substrate (Fig. 2).

Thermal analysis measurements of 4CN type compound were carried out in argon flow atmosphere (150 mL min<sup>-1</sup>), under isothermal and non-isothermal conditions. A horizontal Diamond Differential/Thermogravimetric Analyzer from Perkin-Elmer Instruments was used during the experiments. Samples from 0.8 to 1.2 mg, contained in Al<sub>2</sub>O<sub>3</sub> crucibles, were heated, cooled ( $\beta=10$  K min<sup>-1</sup>) and isothermally kept in the temperature range: 20–1000°C.



**Fig. 2** Principle of MAPLE deposition technique

The films’ surface aspect and roughness were analyzed by atomic force microscopy (AFM) with a Nomad equipment produced by Quesant Instrument Corporation. The thicknesses were evaluated by Spectro-ellipsometry, using a Woollam Variable Angle Spectroscopic Ellipsometer (WVASE) apparatus from J. A. Woollam Co., Inc. The system is equipped with a high pressure Xe discharge lamp, which generates light in the energy range of 1–5 eV from near-IR to UV. Measurements were performed in the UV and near-IR region of the spectrum, between the above mentioned energies, with a step of 0.01 eV, at fixed incident angle of 70°.

The preservation of the obtained structures were checked by FTIR spectroscopy on a Perkin-Elmer Instruments Spectrum 100 apparatus in the range of 550–4000 cm<sup>-1</sup>.

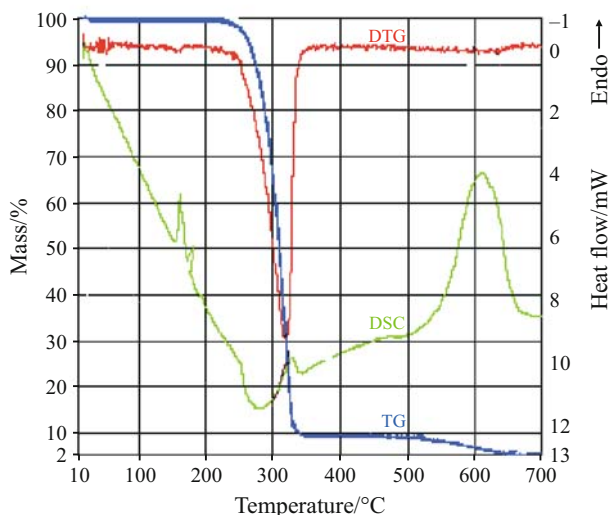
## Results and discussion

### Thermal analysis

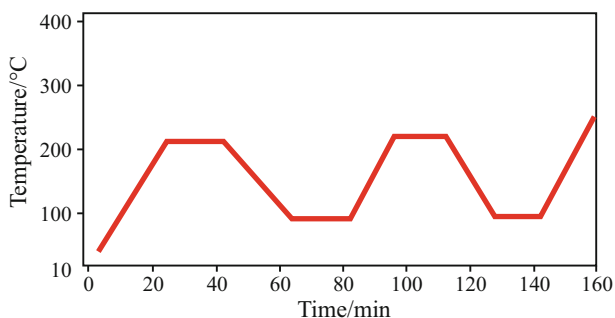
Figure 3 shows the TG, DTG and DSC curves of the investigated compound recorded in argon flow, for the heating rate of 10 K min<sup>-1</sup>. After melting at 158°C and a specific liquid crystalline transition at 195°C, it undergoes endothermic decomposition in the temperature range of 245–350°C (TG curve). The experimental mass loss of the first step ( $\Delta m_{\text{exp}}=91\%$ ) indicates as possible only the entire destruction of all bonds. The remaining 8–9% correspond to the formation of carbon-based residues. The second endothermic process (decomposition of the carbonaceous matter), takes place between 503–665°C.

To establish phase transitions processes, we proposed heating-cooling ( $\beta_h=10$  K min<sup>-1</sup>;  $\beta_c=10$  K min<sup>-1</sup>) explorations, intercalated with 10 min isothermal regimes at 210°C (after heating) and 80°C (after cooling) – Fig. 4.

The heating-cooling cycles reveal two endothermic transformations at heating and three exothermic transformations at cooling, as can be seen in Fig. 5.



**Fig. 3** TG/DTG and DSC curves of 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene (1.1 mg) for the heating rate of 10 K min<sup>-1</sup>



**Fig. 4** Imposed temperature regimes

A DTA-Optical microscope, as described in [15] was used to identify the liquid crystalline mesophases that appear (Fig. 6), first at heating and then at cooling. Between 170 and 220°C, there can be found the liquid anisotropic phase. The investigated compound has Smectic A and Nematic mesophases both at heating and cooling.

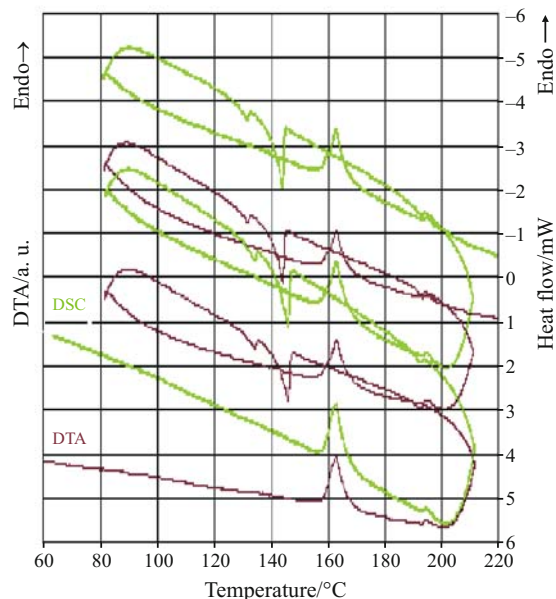
DSC thermal parameters for the heating ( $\beta_h=10 \text{ K min}^{-1}$ ) and cooling ( $\beta_c=10 \text{ K min}^{-1}$ ) are listed in Table 1, respectively in Table 2.

*Thin films – surface morphology*

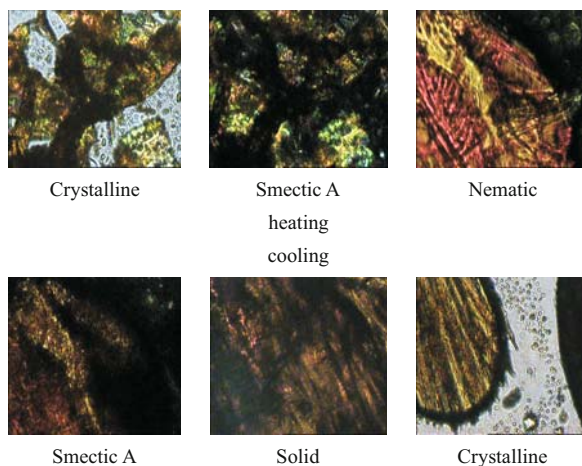
Thin films of our 4CN liquid crystal were obtained on both Si and SiO<sub>2</sub> substrates, for the following

**Table 1** DSC thermal parameters for the heating rate of 10 K min<sup>-1</sup> (heating)

Change	Maximum temperature, $T_{max}/^{\circ}\text{C}$	Temperature range, $T_i-T_f/^{\circ}\text{C}$	Transferred heat, $\Delta H/\text{kJ kg}^{-1}$
Melting (Solid→Smectic A)	158	155–170	102
Phase transition (Smectic A→Nematic)	194	191–196	4
First mass loss	320	265–345	81
Second mass loss	600	503–665	2095



**Fig. 5** Heating-cooling curves of 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene (1.0 mg) for the heating rate of 10 K min<sup>-1</sup>



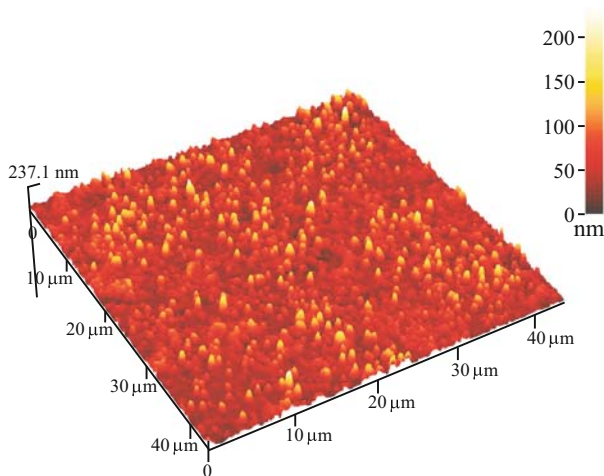
**Fig. 6** Liquid crystalline mesophases of 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene

fluences: 0.066, 0.100 and 0.130 J cm<sup>-2</sup>. AFM images of the films, deposited for 45 min time, reveal continuous and smooth surfaces, when Si was used as substrate (Fig. 7). The roughness of the films deposited on Si increases with the increasing fluence of the laser radiation (from 13.9 nm at 0.066 J cm<sup>-2</sup>, up to 22.3 nm

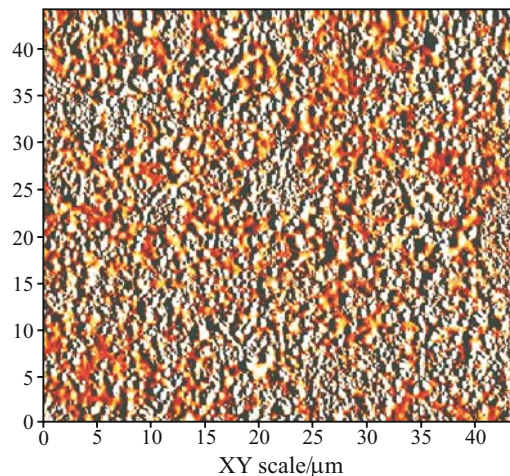


**Table 2** DSC thermal parameters for the cooling rate of 10 K min<sup>-1</sup> (cooling)

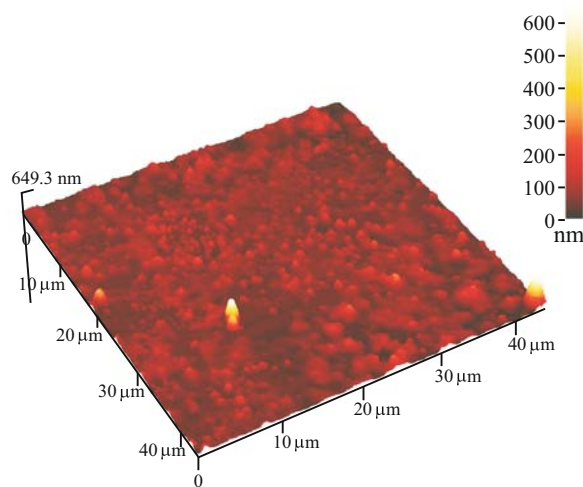
Change	Maximum temperature, $T_{max}/^{\circ}C$	Temperature range, $T_i-T_f/^{\circ}C$	Transferred heat, $\Delta H/kJ\ kg^{-1}$
Phase transition (Nematic→Smectic A)	193	194–189	-6
Solidification (Smectic A→Solid)	146	147–138	-71
Crystallization	133	135–129	-9



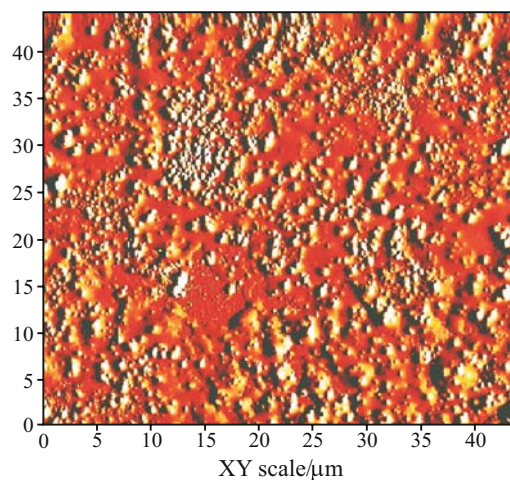
**Fig. 7** 3D image of 4CN layer on Si substrate for a fluence of 0.130 J cm<sup>-2</sup> (after 45 min)



**Fig. 9** 2D image of 4CN layer on Si substrate for a fluence of 0.13 J cm<sup>-2</sup> (after 45 min)



**Fig. 8** 3D image of 4CN layer on SiO<sub>2</sub> substrate for a fluence of 0.130 J cm<sup>-2</sup> (after 45 min)



**Fig. 10** 2D image of 4CN layer on SiO<sub>2</sub> substrate for a fluence of 0.13 J cm<sup>-2</sup> (after 45 min)

at 0.130 J cm<sup>-2</sup>). On a comparison with respect to the depositions on SiO<sub>2</sub> (Fig. 8), the roughness of 4CN thin films on Si substrate is lower (more than 35 nm of organic material on SiO<sub>2</sub> substrate).

2D images (44 μm×44 μm) indicate uniform and compact 4CN layers on Si substrates (Fig. 9), while SiO<sub>2</sub> substrate is not entirely covered (Fig. 10).

On the Si substrates, the growth occurs layer by layer (Frank–van der Merwe mechanism), while on SiO<sub>2</sub> the growth is in patches (Volmer–Weber mecha-

nism) [16]. The crystalline nature and orientation (1 0 0) of Si substrates could be one of the reasons for the better deposition on the surface, when crystalline centres are uniformly attracting the molecules from the plume. Because SiO<sub>2</sub> substrates are amorphous, growth centres may appear in dissimilar high-energy points, caused mainly by defects. This new growth centres (droplets in Fig. 8) are the reason for the attraction of material's molecules and lack of depositions surrounding them.

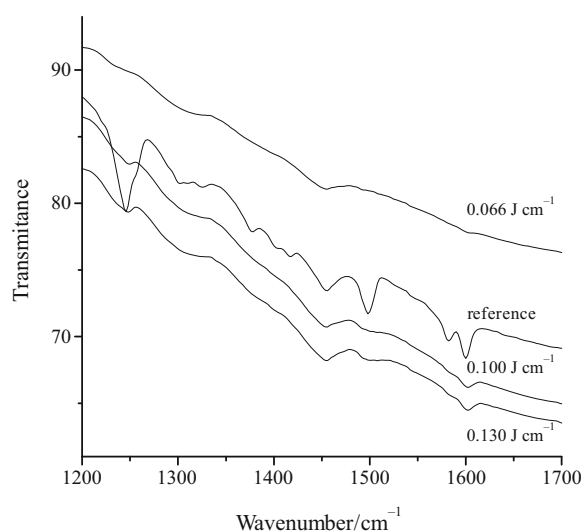
The thickness of the thin film, dependent on the laser energy, can be obtained by spectroellipsometric measurements; in ellipsometry, the change of the polarization state of linearly polarized light is measured upon reflection at the surface. Although spectroellipsometric measurements are simple to be done, data analysis is complicated and requires a complex fitting. In the present work we make use of WVASE32 software, which is designed to handle data modelling and fitting from single film to extremely complex multi-samples and multi-layered problems.

Because the SiO<sub>2</sub> surfaces are not entire covered, experimental spectroellipsometric data are not to be trusted. For our best deposition (substrate: Si, fluence: 0.130 J cm<sup>-2</sup>, deposition time: 45 min) we obtained a thickness of 26 nm.

#### Thin films – chemical profile

FTIR spectra of the obtained thin films were performed in order to identify the compound after the deposition experiments and the best deposition conditions for the growth. The FTIR spectra of the 4CN layers deposited on Si for 45 min are compared in Fig. 11 with the relevant part of the spectra of the compound.

The FTIR analysis confirms the preservation of the compound structure after the transfer, when applying MAPLE technique. For low fluences, the laser is not able to transfer enough material (low intensity peaks), while for the higher fluence (0.130 J cm<sup>-1</sup>) the FTIR curve has almost the same profile with the reference sample.



**Fig. 11** FTIR spectra of 4CN thin films, for different laser's fluences after 45 deposition minutes on Si substrates

## Conclusions

Thermal analysis of a new synthesized liquid crystal: 4-[(4-chlorobenzyl)oxy]-4'-cyano-azobenzene was performed in order to establish its physical transformations (repeated heating-cooling cycles) and thermal stability. MAPLE technique was used to obtain thin films of 4CN type liquid crystal and to surpass the encountered difficulties of PLD concept and procedure. FTIR spectroscopy results indicate the preservation of the initial organic compound on each substrate. On the Si, the growth occurs layer by layer (Frank-van der Merwe mechanism), while on SiO<sub>2</sub> it follows Volmer-Weber mechanism (growth in patches). AFM images reveal continuous and smooth surface for the deposits obtained on Si substrates (increasing together with the laser energy, from 13.9 to 22.3 nm).

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## References

- 1 S. Radu, C. Sarpe-Tudoran, A. Jianu and G. Rau, *Rev. Roum. Chim.*, 43 (1998) 735.
- 2 A. Rotaru, A. Moanta, I. Salageanu, P. Budrugaec and E. Segal, *J. Therm. Anal. Cal.*, 87 (2007) 395.
- 3 A. Rotaru, B. Jurca, A. Moanta, I. Salageanu and E. Segal, *Rev. Roum. Chim.*, 51 (2006) 373.
- 4 M. Gur, H. Kocaokutgen and M. Tas, *Dyes Pigments*, 72 (2007) 101.
- 5 A. Kropidlowska, A. Rotaru, M. Strankowski, B. Becker and E. Segal, *J. Therm. Anal. Cal.*, 91 (2008) 903.
- 6 Y. Sawada, S. Nakazaki, S. Tachibana, Y. Nishimoto and R. Ozao, *J. Therm. Anal. Cal.*, 85 (2006) 57.
- 7 E. Horváth, J. Kristóf, L. Vazquez-Gomez, A. Rédey and V. Vágvölgyi, *J. Therm. Anal. Cal.*, 86 (2006) 141.
- 8 C. Constantinescu, N. Scarisoreanu, A. Moldovan, M. Dinescu, L. Petrescu and G. Epureanu, *Appl. Surf. Sci.*, 253 (2007) 8192.
- 9 N. Scarisoreanu, F. Craciun, G. Dinescu, P. Verardi and M. Dinescu, *Thin Solid Films*, 453 (2004) 3997.
- 10 D. B. Chrisey, A. Pique, R. A. McGill, J. S. Horwitz, B. R. Ringeisen, D. M. Bubb and P. K. Wu, *Chem. Rev.*, 103 (2003) 553.
- 11 C. Constantinescu, N. Scarisoreanu, A. Moldovan, M. Dinescu and C. Vasiliu, *Appl. Surf. Sci.*, 253 (2007) 7711.

- 12 R. Cristescu, E. Axente, G. Socol, A. Moldovan, D. Mihaiescu, I. Stamatina, T. Buruiana, M. Jelinek, I. N. Mihailescu and D. B. Chrisey, *Laser Phys.*, 15 (2005) 1686.
- 13 M. Jelinek, T. Kocourek, J. Remsa, R. Cristescu, I. N. Mihailescu and D. B. Chrisey, *Laser Phys.*, 17 (2007) 66.
- 14 K. Rodrigo, B. Toftmann, J. Schou and R. Pedrys, *Chem. Pys. Lett.*, 399 (2004) 368.
- 15 C. L. Grundner, K. B. Poiesz and N. L. Redman-Fuery, *J. Therm. Anal. Cal.*, 85 (2006) 91.
- 16 J. S. Horwitz and J. A. Sparague, *Pulsed Laser Deposition of thin films*, D. Chrisey and G. Hubler, Eds, New York 1994, pp. 229–235.

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