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MAPLE preparation and characterization of benzil thin films

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In this study the Matrix Assisted Pulsed Laser Evaporation (MAPLE) technique was used to prepare thin films from a low melting point (< 100 °C) organic compound (benzil). Optical properties of the films have been investigated by UV-VIS, FTIR and PL spectroscopy. Details about crystallinity were obtained by XRD measurements. FTIR spectra have confirmed the preservation of the chemical structure of the compound during the deposition process. SEM and AFM investigation have evidenced a topography of the MAPLE deposited films characterized by different grain size depending on the deposition conditions. Second harmonic generation measurements have revealed that the MAPLE deposited benzil films have preserved the optical nonliniar properties of the bulk crystalline benzil.

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1. Introduction

In the last years high interest was paid to the field of the organic materials for electronic and opto-electronic devices as potential candidates for replacing the inorganic materials [1-4]. The main advantage of the organic materials comes out from the compatibility with the flexible substrates making them good candidates for flexible electronics. Many of these compounds are characterized by theoretical high optical nonlinearities and a rapid response in the electro-optic effect representing promising solutions in the field of nonlinear optical materials (NLO) [5-8]. A most organic molecules for nonlinear optics exhibit a system of delocalized π electrons [7, 8]. An advantage of the organic materials over inorganic materials is the possibility to introduce substitution groups to the aromatic nucleus that will disturb the symmetry of the molecule with an important effect on the optical nonlinear response. It was found that the organic materials have parameters competitive with KDP crystals which are the widely used NLO material [9].

Some of the studied NLO organic materials are small molecules aromatic derivatives (e.g. anthracene, meta-dinitrobenzene, benzimidazole, s. o. [8, 10, 11]). One of the small molecule NLO organic materials is benzil [$(C_6H_5CO)_2$] belonging to diketone class and having a skew structure composed from two planar benzoyl units (C6H5-CO) with a 90° dihedral angle between them [12]. Benzil in crystalline state is uniaxial and isomorphic with α-quartz and is known as "organic quartz" [13]. At room temperature benzil crystallizes in the trigonal system and belongs to the D_3^4 ($P3_121$) space group [14]. Also there was found that the benzil has ferroelectric behaviour due to a second order transition at low temperature (83.5 K), which changes the uniaxial form present at room temperature in a biaxial form at low temperature which is favorable for a phase-matching process and for an efficient optical nonlinear effect [15, 16]. Benzil also can be used like dopant for other materials [11, 17].

Crystalline films are preferred for a large scale applications, as a consequence of the complexity and long time involved in the growth of bulk organic crystal. The main experimental difficulties in obtaining good quality organic films arise from specific properties of the organics: low thermal conductivity, anisotropy of growth rate, super cooling phenomenon and low melting point.

In the literature are reported several references for the pure and doped crystalline benzil [18-23], and just a few papers are related to the deposition of benzil thin films by a rapid thermal solidification method between two substrates [15, 24, 25].

The aim of this study is to show that the matrix assisted pulsed laser deposition tehnique can be used for the deposition of benzil thin films with the preservation of the chemical structures and optical nonlinear properties. Because benzil it is a material with a low melting point (< 100 °C) it is difficult to obtain stable thin films by vacuum evaporation.

The properties of the obtained thin films have been investigated using the UV-VIS, FT-IR and Photoluminescence Spectroscopy and the influence of the deposition parameters (fluence, pulses number, etc.) on the properties of the films has been emphasized.

X - Ray - Diffraction gave information on the crystallinity and SEM and AFM microscopy on the morphological particularities of the films.

2. Experimental methods

Benzil thin films depositions were performed in vacuum using an excimer laser source KrF* (λ= 248 nm, τ_{FWHM} = 25 ns) model CompePro 205 from Coherent. The laser beam was focused onto the target surface with a 30 cm focal lenght MgF_2 lens placed outside the irradiation chamber. The laser fluence incident onto the target surface was set at 100 and 190 mJ/cm^2, respectively. For the deposition of the films, we applied up to 65000 subsequent laser pulses, succeeding each other with a repetition rate of 5 Hz. The target was obtained by freezing into liquid nitrogen a solution with the concentration of 5g/l of benzil in dimethyl sulfoxide (DMSO) [Table 1]. In our experiments we used pure crystalline fragment of benzil from the bulk crystalls obtained by the Bridgman-Stockbarger method. Before the growth up the starting material (Aldrich, 98% purity) was purified by zone refining [22].

The films were deposited on Si (100) and fused silica substrates placed at 4 cm from target (Table 1). For the sake of comparision we made a dropcast sample by imersing a cleaned substrate (silicon and fused silica) in above mentioned solution.

UV-VIS optical spectra were measured with a double beam spectrophotometer (GBS, Cintra 10e) in the wavelength range of 190–800 nm, the PL spectra with a Horiba Jobin Yvon Fluorolog 3-22 Spectrofluorimeter and FTIR spectra with a Shimadzu 8400 S Spectrophotometer. The crystalline status of the obtained films was studied by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE diffractometer with Gobel mirror. The XRD diagrams were recorded with the Cu $K_{\alpha 1}$ radiation (λ=1.5406 Å) in the range (2θ) of 5–65° at the grazing incidence, with an angle of incidence set at 2^o, with a step size of 44 seconds per step. The surface morphology of the deposited films was investigated by atomic force microscopy (AFM) in phase feedback mode with a Nanonics 4000 Microscope System and by Scanning Electron Microscopy (SEM) with a Zeiss EVO 50XVP Scanning Electron Microscope. To investigated the optical nonlinear properties of benzil film we used an experimental set-up including a femtosecond pulses laser Spectra Physics "Tsunami" characterized by: maximum emission wavelength 795 nm, pulse duration 60 fs, frequency 80 MHz and average power 780 mW. The laser beam was focused on the sample surface using a high N.A. Mitutoyo microscop objective. The sample was mounted on a motorized Thorlabs XYZ stage.

Table 1. Deposition parameters of MAPLE benzil films.

No.	Sample	Target	Substrate	Temperature [^{o}C]	Pressure [mbar]	Fluence [mJ/cm^2]	Distance [cm]	No. of pulses
1.	Benzil 1	Benzil (5g/l) in DMSO	Si (100) +fused silica	RT	0.08	140mJ/cm^2	4	25000
2.	Benzil 2	Benzil (5g/l) in DMSO	Si (100) +fused silica	RT	0.08	190mJ/cm^2	4	30000
3.	Benzil 3	Benzil (5g/l) in DMSO	Si(100) +fused silica	RT	0.08	100mJ/cm^2	4	65000

3. Results and discussion

MAPLE method is generally used for organic materials thin films deposition because it assures a delicate transfer of the compounds with big molecular mass. The materials can be transfered on a substrare without stoichiometry changes [26]. This time MAPLE method was used for the deposition of a low molecular weight organic compound but with a low melting point..

We have studied the properties of benzil thin films obtained by MAPLE method in conection with the parameters that characteriz the deposition (fluence, number of pulses). The properties of these films have been compared with the properties of dropcast sample. In the Table 1 are given all the depostion parameters.

In Fig. 1 was presented the UV-VIS transmission spectra of MAPLE deposited thin films by comparison with the dropcast film. We can see that by MAPLE we have obtain films with a better transparency (up to 85%) than by dropcasting (~55%) which is important for optical nonlinear applications such as SHG [9]. The reported transparency for the bulk benzil samples was arround 60% [22]. The shape of the absorption edge is determined by the molecular structure of the benzil which can favour a splitting of the (n-π*) level in two components. This splitting is associated to lone pair electrons of the carbonyl groups attached to the aromatic ring [7].

A shift of the fundamental absorbtion edge through a longer wavelength was observed for the sample Benzil 2. This shift is associated with a light scattering phenomenon on the grains of this film. Using a higher fluence for the deposition of Benzil 2 film, we can't rigously control the arrangement of the molecules on the substrate.

The PL spectra for 435 nm excitation wavelength is presented in the Fig. 2 that show that all three benzil films present a large emision band. The emission peak is broadened by the presence of the quartz substrate emission in the low wavelenght range. There are not significantly differences between the photoluminescence properties of benzil as bulk material and films prepared by MAPLE [23]. In benzil the states responsible for emission are the (n-π*) states localized in the carbonyl groups [27] (emission ~ 510 nm). We can conclude that the MAPLE prepared benzil films preserve the emission properties of the bulk material.

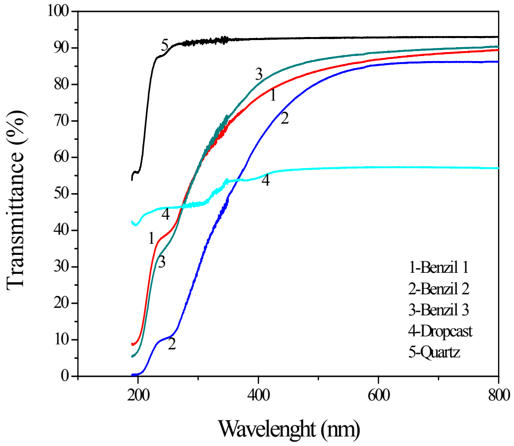

Fig. 1. UV-VIS transmission spectra of MAPLE deposited and dropcast benzil films.

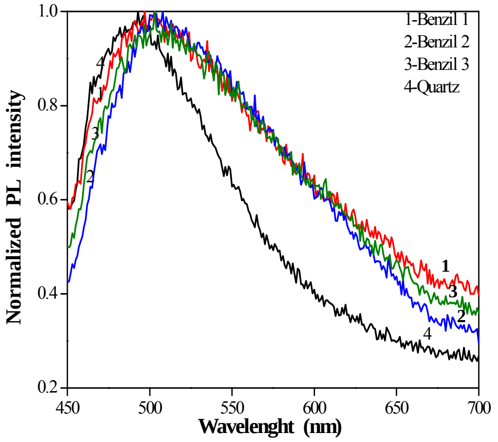

Fig. 2. PL spectra of MAPLE deposited benzil films on quartz, λ_{exc}=435 nm.

The FTIR spectra (Fig. 3) shows that the source material was not decomposed during the deposition process. Many peaks present in the thin film were also found in the dropcast sample, that is a rudimentar tehnhnique and not implies a laser process. This confirm the preservation of the chemical structure for the film prepared by MAPLE, even in the hardest conditions (higher fluence). The 1661 cm^{-1} peak can be atributted to -C=O bond strech, 1591 cm^{-1} peak to -C=C- bond stretch (aromatic) and 700 cm^{-1}, 713 cm^{-1} and 872 cm^{-1} to =C-H bond deformation.

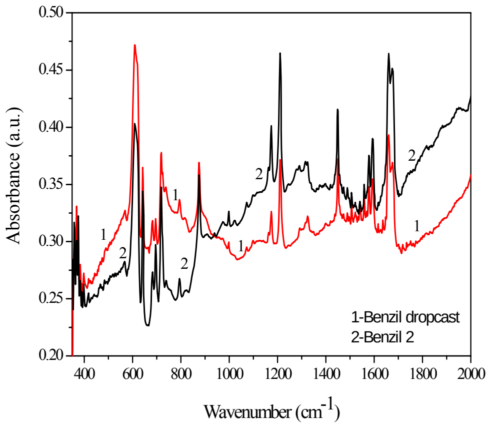

Fig. 3. FTIR spectra of Benzil 2 film by comparission with Benzil dropcast layer.

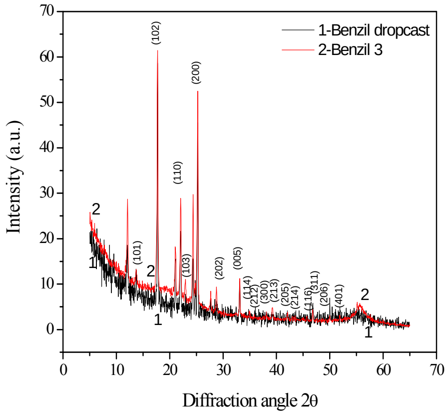

Fig. 4. XRD diagram for Benzil 3 film by comparition with Benzil dropcast layer.

The crystalline quality of the films was investigated by XRD measurements which have evidenced that benzil film is polycrystalline. We have also found many lines which can be associated with benzil powder [28]. The narrow lines present in the MAPLE films XRD spectra sustain that the film presents large size grain. This affirmation is correlated with the SEM images (Fig. 5) and with AFM images (Fig. 6) where we have evidenced grains with different size. In the dropcast film we don't have evidenced diffractions lines because when the films is dryed the molecules are orriented in different directions.

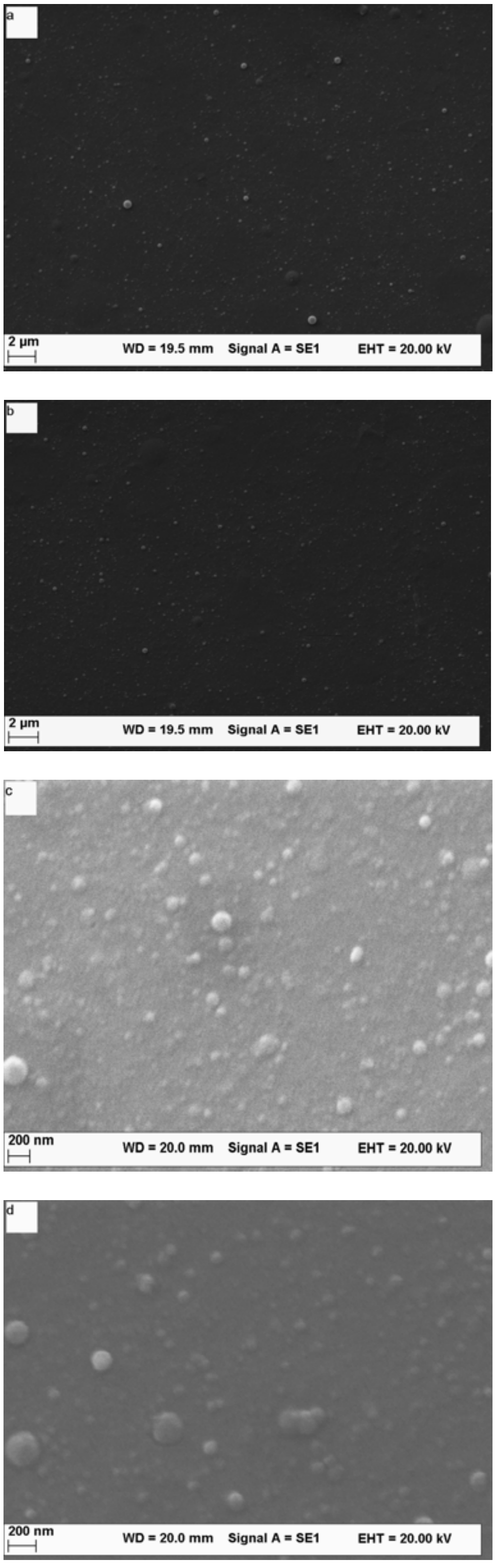

Fig. 5. SEM images of MAPLE films for two different magnitudes: Benzil 2 ((a) and (c)) and for Benzil 3 ((b) and (d)).

MAPLE films are uniform having a grain morphology (Fig. 5) characterized by different sizes. This morphology is different from that of the high weight organic compound deposited by MAPLE that present generaly a „droplet" morphology [29, 30]. The roughness average (deduced from the AFM measurements) for a 10×10 µm scaned aria is R_a=5.8 nm for the film deposited on silicon substrate using a smaller number of pulses (Benzil 1-25000 pulses) and R_a=9.2 nm for the film deposited using a higher number of pulses (Benzil 3-65000 pulses). An increase in the number of pulses used for the deposition of the film leads to an increase in the roughness the film which is correlated with a large size of the grains.

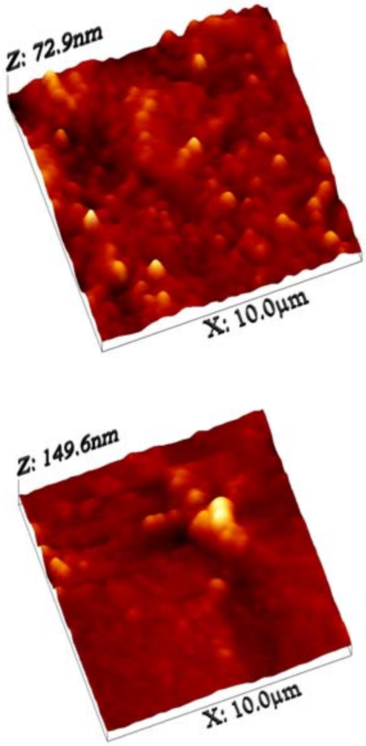

Fig. 6. AFM images of MAPLE (A) Benzil 1film (R_a=5.8 nm) and (b) Benzil 3 film on silicon substrate (R_a=9.2 nm).

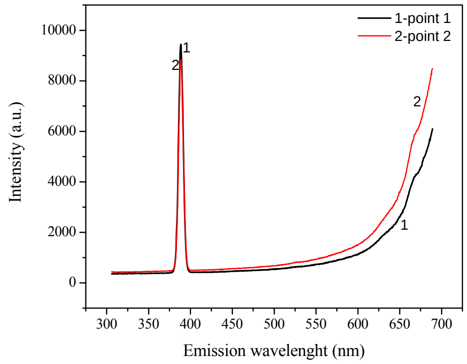

Fig. 7. Non-linear optical effects (SHG) on MAPLE deposited Benzil 2 film.

We have put into evidence the nonlinear optical properties in the MAPLE thin film by measuring the intensity of the second harmonic (SH) in two different points on the Benzil 2 film deposited on Si in the hardest conditions. The emission presented in Fig. 7 confirms the generation of the second harmonic, independent of the laser beam location on the thin film. Si substrate has no contribution to the SH signal. This confirms that the optical nonlinear properties of the material were not affected by using a laser technique to prepare the sample. That means we can deposit benzil thin film without changes in the materials properties.

4. Conclusions

We have used MAPLE for the deposition of benzil thin films, which is an organic compound with a low melting point (<100 ^{o}C) that makes difficult to obtaine thin films by other tehniques. The prepared films are transparent and show a large emission band with a maximum around 510 nm. This behavior is similar to that of the bulk material. The FTIR studies have evidenced that the chemical structure of the source material (powder material) was not deteriorated during the MAPLE deposition. The XRD diagram has shown that the film is polycristalline. The MAPLE deposited films have a morphology confirmed by the SEM and AFM with large grains. The SH measurements have confirmed that the MAPLE deposited benzil films show the same optical nonlinear propertie like the benzil bulk material. As a consequence MAPLE is an adequate tehnique for the preparation low weight organic compound films with the preservation of the molecular structure and, as a consequence, of the optical nonlinear properties.

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