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MAPLE deposited thin monomer films of maleimidic derivatives for photonics

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This paper presents a study of some thin monomer films deposited by MAPLE. These monomers have been synthesised from maleic anhydride and aniline derivatives and are characterized by a molecular structure adequate for the generation of optical non-linear phenomena. UV-VIS, FTIR, Raman and Photoluminescence spectroscopy have been used to investigate the influence of the experimental conditions on the properties of the films. X-Ray Diffraction has evidenced a certain degree of disorder in the thin films, which is correlated with the randomly orientated molecules and AFM images have revealed different roughness for different monomer layers and different substrates. Second harmonic measurements have shown a strong signal emitted by the thin film prepared from the monomer with one [-NH-NH-] donor and two [-NO_2] acceptor groups. This thin film is characterized by good transparency and low photoluminescence emission at excitation with the wavelength of the second harmonic (λ~400 nm).

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1. Introduction

The nonlinear optics includes a large area of investigations from fundamental studies concerning the light interaction with matter to the development of new materials and applications. The photonic technologies are strongly dependent on the materials and involve different aspects: the design at the molecular level, synthesis, investigations of the properties, processing and fabrication of the devices.

Large-capacity optical communications require techniques for measuring high-speed optical signals and techniques for optical switching. The wavelength conversion is based on optical nonlinear crystals characterized by a fast response.

Second order nonlinear optics requires non-centrosymmetric structures, which can be correlated with particular molecular structures [1;3]. Organic materials have relatively strong optical nonlinear properties due to the delocalized electrons in the $\pi - \pi^*$ orbitals and these materials seem to be the key for the development of future photonic technologies [1-4].

Thermally stable π-conjugated molecular structures that contains functional groups with donor and acceptor properties, show large first order molecular hyperpolarizabilities. They are adequate for the generation of optical non-linear phenomena and manufacturing of thin film optical devices for low cost emerging photonic data processing technologies: high bandwidth optical switches and modulators, tuneable wavelength systems filters, small-angle beam steering, remote sensing, photonic control of phased arrays.

Theoretically the optical nonlinear activity can be enhanced by the increase of the strength of the electron donor and/or electron acceptor group, the increase of the length of the conjugated core and the decrease of the ground state aromatic character [5].

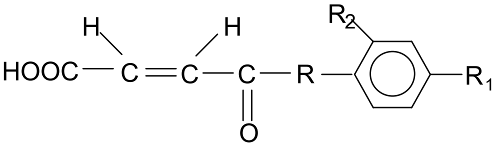
The dipolar segments in the selected maleimidic monomers are characterized by intramolecular donors-acceptors groups: cyano, nitro and carboxyl are electron acceptor groups, and amino is an electron donor (electron withdrawing) group.

The polarity of the monomers molecules depends on the character of the groups that substitute the hydrogen in the benzenic nucleus and on the differences in their electronegativities [6]. As a consequence, the lack of balance or the asymmetry in the distribution of electrons, which is determined by the effect of the substituent groups, induces a polarization with effect on the properties of the molecule.

This paper presents results on the studies of thin monomer films prepared from different dipolar organic monomer compounds. The synthesised monomers are characterized by a maleamic acid structure with different substituent groups [-NH- and COOH/CN/NO_2; -NH-NH- and NO_2, NO_2]. We have investigated the optical properties, crystalline structures and surface morphology of these films as well as the optical nonlinear properties, such as Second Harmonic Generation (SHG).

2. Experimental methods

Firstly we have synthesized the powder of the monomers that will be used for the deposition of the thin films on different substrates:



A1: R=-NH-; R_1=-COOH; R_2=-H;
A2: R=-NH-; R_1=-NO_2; R_2=-H;
A3: R=-NH-; R_1=-CN; R_2=-H;
A7: R=-NH-NH-; R_1=-NO_2; R_2=-NO_2.

We have used to prepare the maleimidic monomners the following starting materials: maleic anhydride (Fluka, 95 % purity) purified by recrystallization in $CHCl_3$, para nitroaniline, para cyano aniline, 2,4 dinitroaniline and 2,4 dinitrophenylhydrazine (all supplied by Fluka, analytical purity) and pamino benzoic acid [7; 8].

Details about the route of synthesis implying the opening of the anhydridic cycle in dimethylformamide (DMF), precipitation in ice, filtration and recrystallization from methanol have been previously given [8].

Matrix Assisted Pulsed Laser Evaporation (MAPLE) has been used to prepare thin films of these monomers on single crystal substrates: (100) double side polished silicon and (001) quartz, which have been previously cleaned ultrasonically in acetone and alcohol ethylic with a Transonic T310 bath [7].

MAPLE is a version of the Pulsed Laser Deposition (PLD), which uses as target a frozen solution of the molecules to be deposited in a highly volatile and light absorbing solvent. In our case, the solution of the monomer in dimethylsulphoxide (DMSO) is frozen in liquid nitrogen and the resulted target is placed inside the vacuum chamber. The MAPLE experimental configuration is composed of an excimer KrF* laser (λ=248 nm), a pulse duration monitorization set-up, a focalisation system based on a MgF_2 lens and a substrate temperature controller. The target is rotated to avoid its deterioration, which could affect the deposition parameters and, consequently, the quality of the layer. The laser beam energy is converted into thermal energy that generates the vaporization of the solvent and monomer molecules forming a plume. The vacuum pumping system removes the volatile molecule of solvent while the organic molecules deposit onto the substrate situated at a given distance from the target for a given deposition geometry. Details about the experimental configuration are presented in previous papers [7; 8].

The experimental parameters, which can be changed are: the target composition, substrate temperature, substrate-target distance, atmosphere in the deposition chamber, fluence and number of pulses.

Table 1. Maple experimental deposition conditions for maleimidic monomers.

Sample monomer/substrates	Temperature [ºC]	Pressure [mbar]	Thickness of the thin films deposited on Si substrate [nm]
A1-1/Si; quartz	200	0,07	18
A1-2/Si; quartz	200	0,07	11
A1-3/Si; quartz	200	0,07	55
A1-4/Si; quartz	150	0,3 N_2	140
A1-5/Si; quartz	200	0,3 N_2	74
A2-1/Si; quartz	200	0,07	23
A2-2/Si; quartz	100	0,07	98
A2-3/Si; quartz	200	0,3 N_2	111
A3-1/Si; quartz	200	0,07	13
A3-2/Si; quartz	200	0,3 N_2	14
A7-1/Si; quartz	150	0,07	33
A7-2/Si; quartz	150	0,3 N_2	45

Because the organic compounds are very photosensitive and can be decomposed under the laser beam action we have used low fluence of 430 mJ/cm^2 (for A1 samples) and 350 mJ/cm^2 (for A2, A3 and A7 samples) with the purpose to preserve the molecular structure. The deposition took place in vacuum (0.07 mbar) or nitrogen (0.3 mbar). The nitrogen background gas assures the thermalisation of the molecules and the control of the deposition process. For all the experiments the distance substrate-target was 4 cm, the target concentration was 2.2 wt % (excepting the sample A1-1 for which was 1.1 wt %) and the number of pulses was 20 000 (excepting the sample A1-3 for which was 30 000).

The monomer layers (Table 1) have been characterised by UV-VIS spectroscopy using a Double beam CINTRA 10e GBC Spectrophotometer, Fourier Transform Infrared (FTIR) spectroscopy using a Shimadzu 800 Spectrophotometer, Raman spectroscopy using a Bruker RFS 100 Spectrometer (experimental conditions: $\lambda_{excitation}$=1064 nm; P_{maxim}=250 mW; resolution=4 cm^{-1} to assure a good ratio signal-noise, no.scans/sample=256), Photoluminescence spectroscopy using a Horiba Jobin Yvon Fluorolog 3-22 Spectrofluorimeter (experimental conditions: 1. $\lambda_{excitation}$=435 nm; λ=450-850 nm; 2. $\lambda_{excitation}$=385 nm; λ=400-755 nm).

A spectro-ellipsometer J. A. Woolam WASE 32 was used for the evaluation of the thickness of the layers deposited on Si substrate in the following experimental conditions: λ=190-1340 nm, $\theta_{incidence}$=65^o-70^o or 70^o-75^o, spectral resolution=10 nm. The experimental data have been analysed with the Cauchy dispersion formula [9].

The morphology of the thin films surface was analyzed by AFM measurements with a MultiView 4000 Nanonics System.

The structure of the layer was investigated by X-ray Diffraction measurements with a Brucker D8 Advance Diffractometer using the Cu $K_{\alpha 1}$ line at the grazing incidence, with an acceleration voltage of 40 kV and an anodic current of 40 mA.

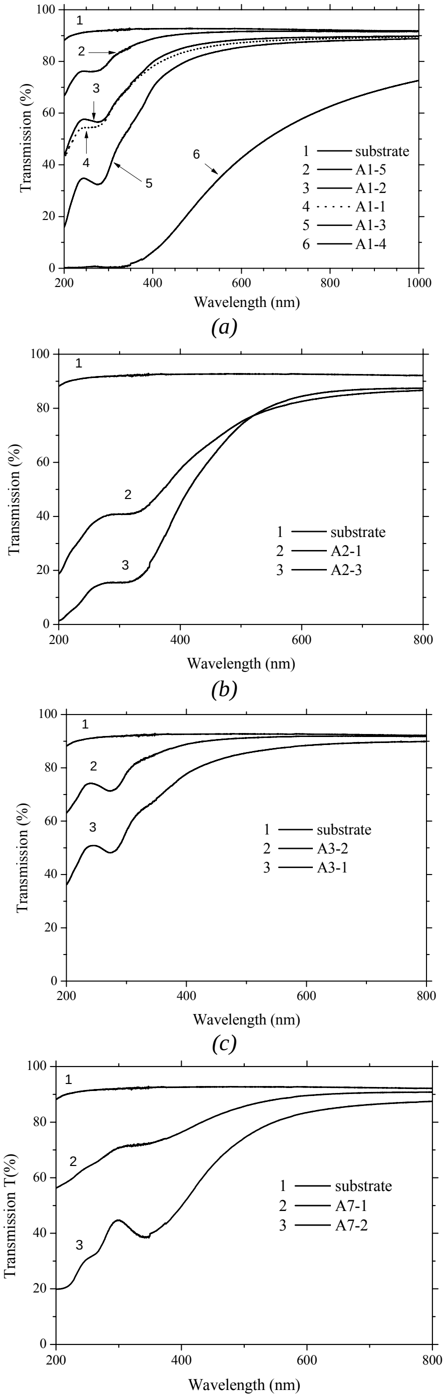
The experimental set-up for measuring the second harmonic (SH) intensity has been presented in a previous paper [8]. An ultrashort pulsed laser Spectra Physics "Tsunami" with λ_{max}=800 nm, pulse duration 60 fs, frequency 80 MHz, medium power 780 mW was used for the generation of the second harmonic. To focus the laser beam we have used a high N.A. Mitutoyo microscope objective. This objective has also been used for the collection in the 180° geometry, of the emitted light. The sample was moved with a motorized Thorlabs XYZ stage. The light has passed through a dichroic mirror and was focused by the lens on the collecting optical fiber of the spectrograph ANDOR Shamrock 163i. An ANDOR IDUS CCD camera, cooled at 213 K, has measured the dispersed light. The NIR cut-off filter mounted in front of the focalisation lens assures the optimisation of the detection system and the increase in the amplification of the CCD detector [8].

3. Results and discussion

The UV-VIS, FTIR Raman and Photoluminescence spectroscopy, XRD and AFM measurements have been utilized to characterize the monomeric films with thickness between 11 nm and 140 nm and analyse the influence of the deposition parameters such as temperature, atmosphere (vacuum; nitrogen), fluence, pulses number and target concentration on the properties of the films.

A comparative study of the UV-VIS spectra of the thin monomer films (Fig. 1 (a), (b), (c), (d)) has evidenced, for most of the films, a large transparency domain (200-800 nm). The absorption edge shows a shoulder between 200 nm and 300 nm. This specific shape is associated with the splitting into two bands of the (n, π*) level [10] of the dicarbonyl or/and nitrous groups, which are strongly interacting in the thin films. The (n, π*) level is correlated with the presence of the lone electron of the O and/or N atoms [7;11]. All of the thin monomer films (excepting A1-4) show a transparency >60 % in the visible range at λ>400 nm (Fig. 1 (a)).

We have not evidenced significant changes in the shape and the level of the transparency of the MAPLE prepared thin films (Fig. 1 (a)) with the modification of the concentration of the A1 monomer in DMSO. For a given monomer, A1, the lowest transparency (Fig. 1 (a)) was obtained for the film (A1-4) prepared in a nitrogen atmosphere (0.3 mbar) at lower temperature of the deposition substrate (150 °C).



(a)

(b)

(c)

(d)

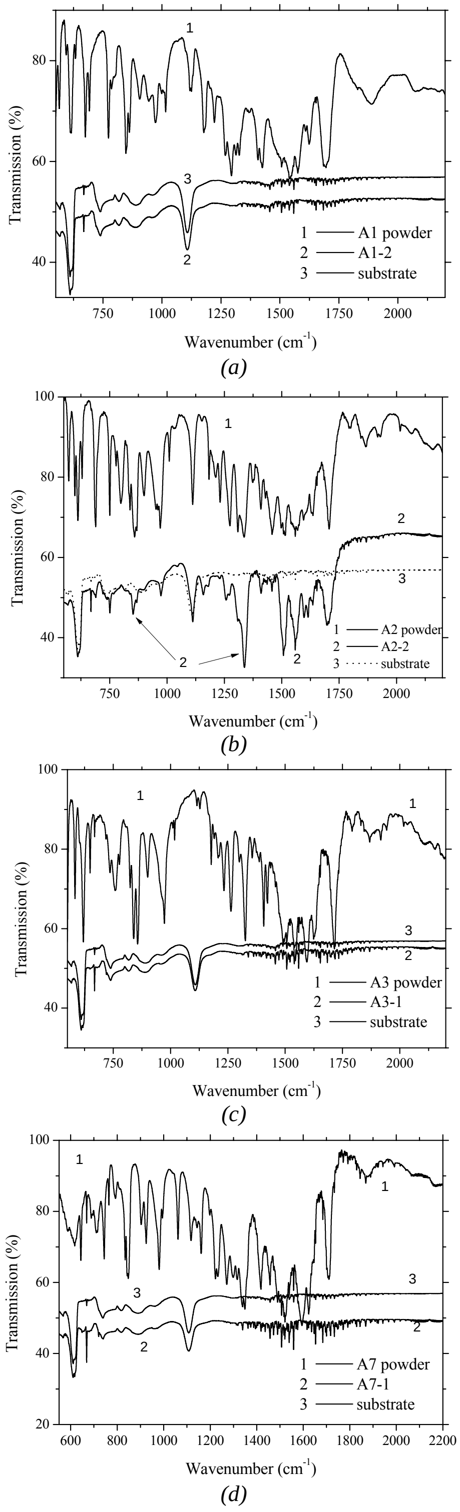
Fig. 1. UV–VIS transmission spectra of thin monomer films: (a) thin A1 monomer films prepared in different experimental conditions; (b) comparative spectra of thin A2 monomer films prepared in vacuum and nitrogen atmosphere; (c) comparative spectra of thin A3 monomer films prepared in vacuum and nitrogen atmosphere; (d) comparative spectra of thin A7 monomers films prepared in vacuum and nitrogen atmosphere.

The other experimental parameters, the target concentration (2.2 wt %), fluence (350 mJ/cm^2) and number of pulses (20 000), have not been changed. The nitrogen affects the optical properties by the molecule thermalisation (Fig. 1 (a), (b)), mechanism that controls the deposition process and the quality of the layer. A decrease in the fluence and increase in the number of pulses, for the same concentration of the target, determines an increase in the thickness of the layer (Fig. 1 (a), Table 1).

The laser techniques are difficult to apply for the deposition of organic compounds thin films because they chemical bounds are very weak and can be easily broken inducing a chemical deterioration of the compound. The chemical composition of the layer can be also changed by nitrogen incorporation. The influence of the deposition method on the chemical composition of the films can be investigated by FTIR spectroscopy.

For each monomer we have comparatively studied the FTIR spectra for the powder and thin films deposited in vacuum and in nitrogen atmosphere. Well defined peaks have been evidenced on the powder of monomers: A1; A2; A3; A7 (Fig. 2 (a), (b), (c), (d)). We have evidenced the presence of the moderate or strong characteristic bands for the following sequences in aromatics, carboxyl acids and amides: [-NH-] group (1640 cm^{-1}; 1540 cm^{-1} [12]), [-C=O] group (1250 cm^{-1} [13-15]), [-CN] group (~1240 cm^{-1} [16]), [-CH=CH-] double bound (~840 cm^{-1} [13-15]) and [-C-H-] single bound (640 cm^{-1} [13-15]). We have also remarked the presence of the characteristic bands for amides situated at 1390 cm^{-1} [17] and imides ring deformation situated at 1100 cm^{-1} and 730 cm^{-1} that sustain the simultaneous presence of the amidic and imidic form of the monomer [18]. The bands situated in the range 650-800 cm^{-1} can be attributed to substituted benzene and those situated in the range 1250-1300 cm^{-1} to the symmetric stretching vibration of [-NO$_2$] [13-15].

Most of the peaks present in the FTIR spectrum of the monomer powder have disappeared in the FTIR spectrum of the films because the films are very thin. The FTIR spectra (Fig. 2 (a), (b), (c), (d)) show mostly the absorption peaks associated to the Si substrate. The shift of the curve on the y-axe is correlated with the slit size and position. The shift was intentionally increased to evidence the shape of the spectrum for Si substrate and thin monomer film on Si substrate. Other peaks have become weaker and broader because the molecules are strongly interacting in the solid state.



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(d)

Fig. 2. FTIR spectra of monomers powder and thin films deposited by MAPLE: (a) comparative spectra of A1 monomer powder and thin films deposited in vacuum; (b) comparative spectra of A2 monomer powder and thin films deposited in vacuum; (c) comparative spectra of A3 monomer powder and thin films deposited in vacuum; (d) comparative spectra of A7 monomer powder and thin films deposited in vacuum.

The A2 monomer thin films deposited in vacuum (Fig. 2 (b)) preserve most of the absorption peaks of A2 powder, which are situated between 600 cm^{-1} and 1800 cm^{-1}. This sustains that during the MAPLE process the chemical structure is not destroyed (Fig. 2 (b)).

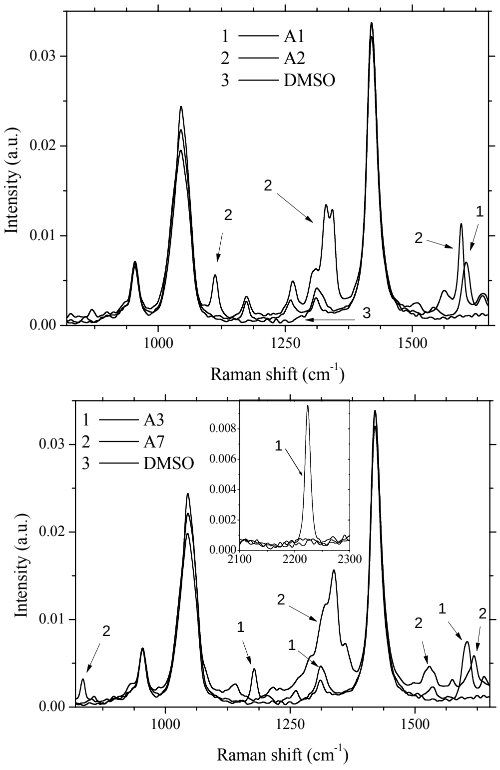
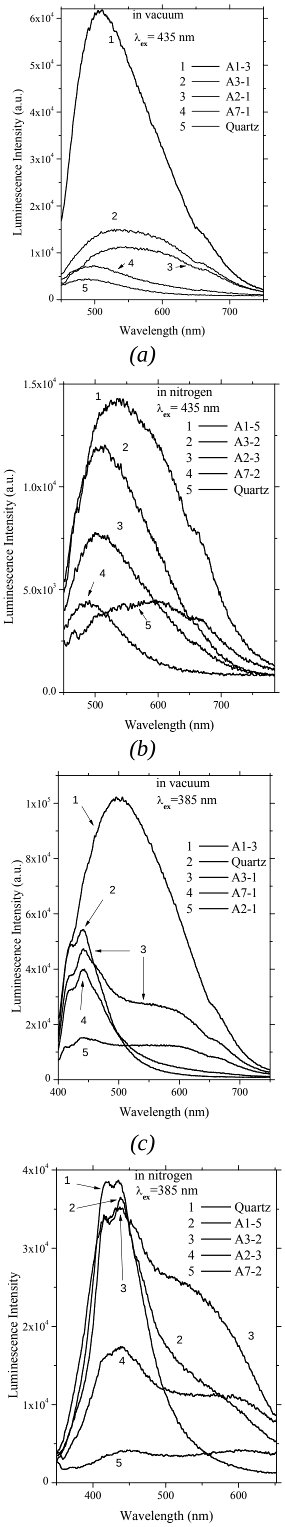


Fig. 3. Raman spectra on solutions of A1, A2, A3 and A7 monomers powder in DMSO.

The Raman spectra have been obtained on the solution used for the preparation of the MAPLE target: monomers in DMSO. Most of the well-defined peaks (Fig. 3) situated between 800 cm^{-1}and 1750 cm^{-1}, are correlated with the scattering on internal vibrational modes and could be associated with the deformation of the molecules. The differences in the spectra (Fig. 3) are the Raman shift peaks corresponding to the different substituents to the aromatic ring [19]: [NO_2] group stretching vibration in A2, and A7, around 1340 cm^{-1}; [CN] group stretching vibration in A3 around 2220 cm^{-1}. The A7 monomer characterized by a tri-substituted benzene ring shows Raman shift peaks situated around 834 cm^{-1} and 1530 cm^{-1}. All the monomers show a peak around 1600 cm^{-1} that corresponds to the double bound –C=C- stretching vibration [19]. We have not evidenced peaks between 75 cm^{-1} and 100 cm^{-1}, which could be attributed to the external vibrations correlated with the relative rotational or translational movement of the molecules in solution.

Raman shift peaks have not been evidenced on the monomer films (thickness <150 nm) because they are too thin to generate a significant signal.



(a)

(b)

(c)

(d)

Fig. 4. Photoluminescence spectra of A1, A2, A3 and A7 monomer thin films: a) thin monomers films deposited in vacuum, $\lambda_{excitation}$=435 nm; (b) thin monomers films deposited in nitrogen, $\lambda_{excitation}$=435 nm; (c) thin monomers films deposited in vacuum, $\lambda_{excitation}$=385 nm; (d) thin monomers film deposited in nitrogen, $\lambda_{excitation}$=385 nm.

The photoluminescence spectra of A2 and A3 thin films prepared in vacuum, for an excitation wavelength situated in visible, $\lambda_{excitation}$=435 nm (Fig. 4 (a)), show a broad band centered around 550 nm. The asymmetry of the spectra at λ>600 nm suggests the existence of an unsolved local maximum. The monomer A1 thin film prepared in vacuum shows a narrow peak centered at 510 nm and a shoulder at λ> 600 nm. The monomer A7 thin film photoluminescence is weak and difficult to separate by the photoluminescence of the quartz substrate. Under the same excitation wavelength, the thin films prepared in nitrogen atmosphere show (Fig. 4 (b)), an emission band more asymmetric with the maximum slightly moving towards longer wavelength in the succession: $\lambda_{max}(A1)<\lambda_{max}(A3)<\lambda_{max}(A2)$. The emission of monomer A7 thin film is a broad weaker band situated between 450 nm and 700 nm. The photoluminescence is a phenomenon important in materials for nonlinear optics because it can partially consume the SH intensity. This could happen when the photoluminescence signal is generated by an excitation wavelength close to the wavelength of the SH and the material shows a significant absorbance at this wavelength. As a consequence the SH signal becomes weaker because it is partially reabsorbed. On the other hand a significant photoluminescence around 400 nm can screen the SH signal. To analyze this emission phenomenon affecting the optical non-linear properties of the monomers we have studied the emission at different excitation wavelengths (435 nm and 385 nm). The most important is the photoluminescence emission at $\lambda_{excitation}$=385 nm, which is close to the λ_{SH}=400 nm. In this case, the monomers A3 and A7 films prepared in vacuum (Fig. 4 (c)) have shown a narrow photoluminescence peak at λ=450 nm, which is difficult to separate by the quartz substrate contribution. The A1 monomer thin film has shown a narrow and stronger emission peak centered at 510 nm and A2 monomer film a weak broad band in the range 400-700 nm. For this excitation wavelength the behaviour is different for the films prepared in nitrogen. All the samples show a peak situated at 450 nm and a partially unsolved emission band situated at λ>550 nm (Fig. 4 (d)). The A7 monomer thin films prepared in vacuum and nitrogen have shown a low photoluminescence in visible at the mentioned excitation wavelengths.

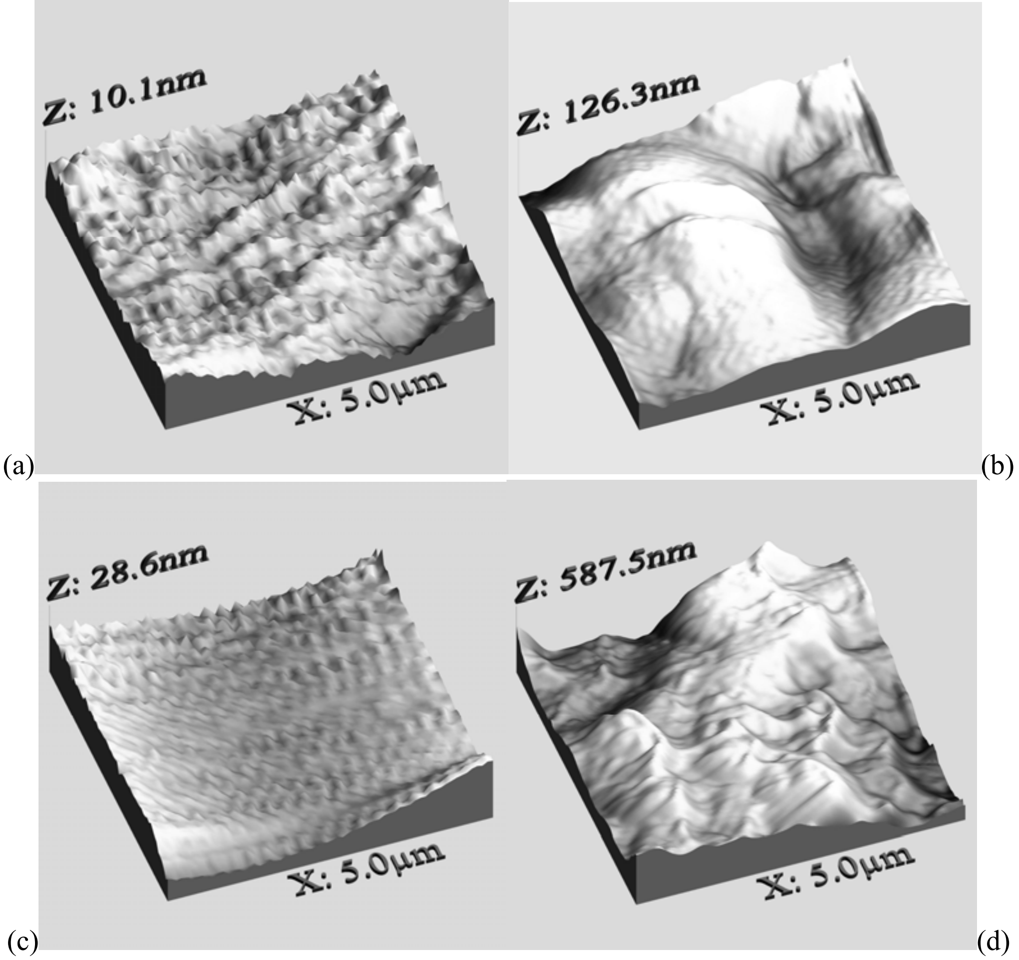


Fig. 5. (a) AFM image of quartz substrate: area of 5.0 µm×5.0 µm; vertical scale of 10.1 nm; (b) AFM image of thin A7 film on quartz: area of 5.0 µm×5.0 µm; vertical scale of 126.3 nm; (c) AFM image of Si substrate: area of 5.0 µm×5.0 µm; vertical scale of 28.6 nm;(d) AFM image of thin A2 film on Si: area of 5.0 µm×5.0 µm; vertical scale of 587.5 nm.

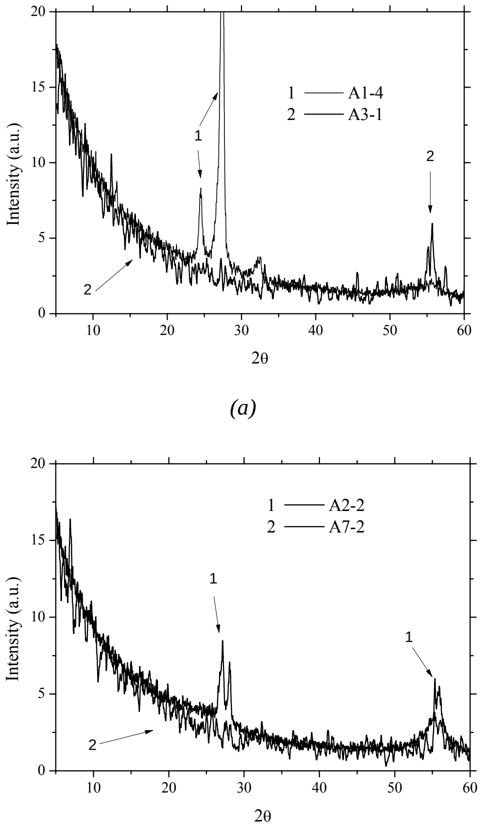
The optical properties are influenced by the quality of the organic layer revealed by its morphology and structure. Therefore we have studied the morphology of the monomer film on quartz/silicon substrate by comparison to the morphology of the substrate. We have evidenced a mountain-valley structure associated with a higher roughness of the investigated monomer A7/A2 (Fig. 5 (b), (d)) compared to the roughness of the quartz/Si substrate (Fig. 5 (a), (c)). The parameters for the A1, A7 and A3 films, the root-mean-square roughness (RMS) of 37 nm, 23 nm and 15 nm respectively and the roughness average (RA) of 31 nm, 19 nm and 11 nm respectively, sustain a lower roughness of the A3 layer compared to A1 and A7 layer. The AFM image of the quartz substrate has revealed a (RMS)=1.24 nm and (RA)=0.95 nm indicating a very smooth surface.

The parameters for the A2 film, the root-mean-square roughness (RMS) of 102 nm and the roughness average (RA) of 82 nm sustain a high roughness of the A2 layer deposited on Si. The AFM image of the Si substrate has revealed a (RMS)=3.39 nm and (RA)=2.73 nm indicating a rougher silicon surface compared to quartz surface.

X-Ray Diffraction spectra (Fig. 6 (a), (b)) of thin A1, A2, A3 and A7 monomer films have shown a diffraction peak at 55^o, independent of the deposition substrate. Other diffraction peaks are missing in A3 and A7 monomer films and this suggests that the films are, in a certain degree, amorphous or the molecules are randomly oriented, inducing disorder states in the thin films [20; 21]. Narrow strong peaks have been evidenced at 22.72^o, 27.36^o and a broad lower peak at 32.48^o for A1 monomer deposited on quartz. A splitted peak has also been evidenced around 27-28^o for A2 monomer film deposited on Si. This shape of the X-Ray spectra has indicated a crystalline order in A1 and A2 films. These results are in concordance with the (RMS) and (RA) values obtained for the monomers films presented above. We have revealed the largest grain size structure for A2 monomer thin film deposited by MAPLE on Si. For the sample deposited by MAPLE on quartz the largest grain size structure was evidenced for monomer A1 thin film.

The optical non-linear phenomena are determined in the first place by the molecular structure of the compounds, which is correlated with the substituent groups that interact with the delocalised π electrons, and with the difference in the electronegativity between the donor [-NH-; -NH-NH-] and acceptor [-NO_2; -CN] substituent groups [22].

From theoretical considerations the strongest non-linear effect was associated with the A2 and A7 monomers because the strength of the acceptor group [-NO_2] is higher than of [-CN] or [-COOH] groups and varies in the succession NO_2>CN>COOH [23]. These compounds are based on polarisable [-NO_2] and [-NH-/-NH-NH-] substituent groups with high differences in electronegativities that are coupled with the polarisable aromatic nucleus and are characterised by high optical polarizability and relatively high dipole momentum. It is expected to evidence a stronger optical non-linear phenomenon, such as SHG, in A7 monomer thin film, compared to A2 monomer thin film. A7 monomer has beside the [-NH-NH-] electron donor and [-NO_2] electron acceptor groups situated on opposite sides of the molecules (para substitution) a supplementary nitro group situated in ortho position that breaks the centrosymmetry of the electronic cloud and favours the SHG.



(a)

(b)

Fig. 6. XRD spectra for thin monomers films: (a) A1/quartz and A3/quartz; (b) A2/Si and A7/quartz.

The SH emission (Fig. 7) was evidenced in thin films of the A7 monomer based on maleic anhydride and 2,4 dinitroaniline. For a correct assignment of the emission peak of the thin monomer film deposited on quartz, situated at 400 nm, for a laser excitation wavelength λ=800 nm, we have also measured the SH on the monomer powder (Fig. 7). The powder was placed on an aluminium substrate that has no contribution to the SH emission.

From these considerations, the most adequate thin monomer film for optical non-linear applications is A7 film, which is characterized by an adequate molecular structure and good physical properties such as good transparency and low photoluminescence in the region of SH emission for $\lambda_{excitation}$ around 400 nm.

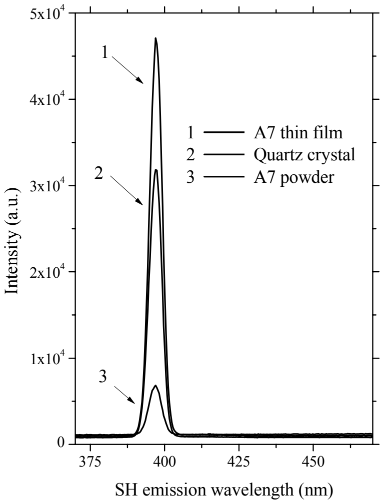


Fig. 7. SH spectra of A7 thin film deposited on quartz.

4. Conclusions

This paper presents the preparation and characterisation of some thin films of dipolar organic monomeric compounds and proposes a thin monomer film for applications in non-linear optic for Second Harmonic Generation.

Four monomeric structures characterized by a maleamic acid structure, containing different donor [-NH-, -NH-NH-] and acceptor [-COOH, -CN, -NO_2] groups have been synthesised from maleic anhydride and some aniline derivatives.

These monomers have been used to prepare by MAPLE on silicon and quartz substrates films of different thickness (11-140 nm), morphology and structures. The influence of the deposition conditions (target concentration, substrate temperature, fluence, number of pulses and atmosphere in the deposition chamber) on the properties of the thin films has been studied.

A comparative study of the UV-VIS spectra of the thin monomers films has evidenced, for most of the samples, a large transparency domain (200-800 nm) and a transparency >60 % in the visible range. The substrate temperature has an important influence on the film properties. The transparency of the film prepared in nitrogen atmosphere has reduced when the substrate temperature has decreased, for the same concentration of the target, fluence and number of pulses.

We have also investigated the photoluminescence emission of the thin monomer films in the visible range for an excitation wavelength close to the wavelength of the SH (λ_{SH}=400 nm).

The thin film of monomer A7 containing one [-NH-NH-] donor group and two [-NO_2] acceptor groups is the most adequate for optical nonlinear application despite a certain degree of disorder and relatively low grain size structure. It combines the advantageous molecular structure of the monomer that implies high optical polarizability and high dipolar momentum with the good transparency and weak photoluminescence emission in visible, which prevent the reabsorption of the SH and the decreasing/screening of the SH signal.

Acknowledgements

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