# PHOTONIC DEVICES BASED ON PATTERNING BY TWO PHOTON INDUCED POLYMERIZATION TECHNIQUE

I.Fortunati[a]; T.Dainese[a]; R.Signorini[*a]; R.Bozio[a]; V.Tagliazucca[b]; S.Dirè[b]; G.Lemercier[c]; J.-C. Mulatier[c]; C.Andraud[c]; P.Schiavuta[d]; A.Rinaldi[e]; S.Licoccia[e]; J.Bottazzo[f]; A.Franco Perez[f]; M.Guglielmi[f]; G.Brusatin[f]
[a]Dept. of Chemical Science, Univ. of Padova, Via Marzolo 1, 35131, Padova, Italy;
[b]Dept. of Mat. Eng. and Ind. Techn., Univ. of Trento, via Mesiano 77, 38050 Trento, Italy
[c]Lab. de Chimie, CNRS/ENS-Lyon, 46 Allee d'Italie, 69364 Lyon Cedex 07, France
[d]Ass. Civen-Nanofabrication Facility, via delle industrie 9, 30175, Marghera, Venezia, Italy
[e] NAST Centre for Nanoscience & Nanotechnology & Innovative Instrumentation and Department of Chemical Science and Technologies, Univ. of Rome TorVergata, 00133 Roma, Italy
[f]Dept. of Mech. Eng.-Materials Section, Univ. of Padova, Via Marzolo 9, 35131, Padova, Italy

## ABSTRACT

Two and three dimensional structures with micron and submicron resolution have been achieved in commercial resists, polymeric materials and sol-gel materials by several lithographic techniques. In this context, silicon-based sol-gel materials are particularly interesting because of their versatility, chemical and thermal stability, amount of embeddable active compounds. Compared with other micro- and nano-fabrication schemes, the Two Photon Induced Polymerization is unique in its 3D processing capability. The photopolymerization is performed with laser beam in the near-IR region, where samples show less absorption and less scattering, giving rise to a deeper penetration of the light. The use of ultrashort laser pulses allows the starting of nonlinear processes like multiphoton absorption at relatively low average power without thermally damaging the samples.

In this work we report results on the photopolymerization process in hybrid organic-inorganic films based photopolymerizable methacrylate-containing Si-nanobuilding blocks. Films, obtained through sol-gel synthesis, are doped with a photo-initiator allowing a radical polymerization of methacrylic groups. The photo-initiator is activated by femtosecond laser source, at different input energies. The development of the unexposed regions is performed with a suitable solvent and the photopolymerized structures are characterized by microscopy techniques.

**Keywords:** Two-photon photopolymerization, (meth)acrylic units, nanobuilding blocks, sol-gel, microscopy.

## INTRODUCTION

The possibility to create novel micro- and nano-structured materials has attracted great attention in scientific community. Among the nanofabrication methods, the non-linear optical lithographic technique, called Two Photon Induced Polymerization (TPIP), and based on two-photon absorption (TPA) in a photosensitive material, is a powerful tool to obtain 2D and 3D structures. This technique offers multiple advantages, including spatial and temporal controls, fast curing speed at room temperature, large efficiency and great versatility of the composition of the initial prepolymer blend.

The photopolymerization process, initiated by non-linear absorption of tightly focused ultrashort laser pulses, is well confined within the focal volume. The extension of the excited region, below the sub-diffraction limit spatial resolution, is determined by the dimension of the focused beam.[1,2] By moving the sample in 3D directions, it is possible to create

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[*] raffaella.signorini@unipd.it; phone +39 0498275118; fax +39 0498275239

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the desired pattern within samples. Generally, in a second step, the unexposed regions are washed away with a suitable developer. Several groups have utilized this process to write 3D photonic band gap structures or to realize 3D optical memories.[3-8]

Materials commonly used as photoresists for TPIP are organic polymers: a great variety of prepolymer resists have been studied.[9,10] In many works, the photoactive units are (meth)acrylates, undergoing free-radical polymerization, activated through photoinitiators by mean of adequate wavelength sources. This mechanism is severely inhibited by atmospheric molecular oxygen that causes numerous effects, including slow polymerization rates, low conversion and short polymer chain length.[11] We have recently reported some results confirming that this is an important feature when one-photon polymerization experiments are performed.[12]

FT-IR[1,13,14] and real time Raman[15] spectroscopies are the main techniques to investigate the rate and the efficiency of the photopolymerization processes.

In this contribution we report on preliminary results using new materials obtained from hybrid organic/inorganic sol-gel precursors. The sol-gel chemistry, based particularly on the use of hybrid organic/inorganic materials, is largely exploited to design a large variety of novel materials, with controlled micro- and nano-structures. The final sol-gel materials often possess superior properties with respect to polymers, such as high optical properties, good mechanical and chemical resistance (like superior resistance against dry etching processes and scratch) and the possibility of embedding large amounts of active compounds[16,1718].

In particular, we explore the use of Si-based nanobuilding blocks (NBBs) to improve the spatial resolution of the photopolymerized structures.[19,20,21,22] These nanosized objects, containing lateral acrylate groups, suitable for polymerization, are obtained by the condensation reaction between $Ph_2Si(OH)_2$ (diphenylsilanediol, DPDO) and methacryloxypropyltrimethoxysilane (MPTMS) in controlled synthetic conditions, exploiting the in-situ water production by means of an esterificatione reaction.[23] It is recognized that the very low hydrolysis ratio and the strict control on hydrolysis –condensation process achieved through this approach is useful to obtain an almost complete reaction between the Si-OH and the Si-OR groups of the precursors reaching a good yield in cyclosiloxane-based oligomers.

Our research is aimed at the production of well condensed hybrid precursors containing a large amount of double bonds useful for an efficient photopolymerization process. The photopolymerization experiments are performed with a femtosecond laser source, employing a focusing set-up with 0.55 and 0.8 numerical aperture long working distance. The obtained structures are analyzed by confocal optical microscopy, scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM).

## METHODOLOGY

### 2.1 Synthesis of sol-gel samples

The synthesis of the NBBs is achieved by mixing the DPDO (2.5 mmol, 0.5408 g), MPTMS (12.5 mmol, 2.971 ml), $CH_3COOH$ (AA) (5 mmol, 0,286 ml) and ethanol (10 mmol, 4.06 ml). The molar ratio is: DPDO:MPTMS:AA:EtOH = 1:5:2:4. The viscous yellowish solution, obtained after stirring for 14 days at 75°C, is evaporated to dryness and diluted with dry THF to a desired final concentration.

For the preparation of the photosensitive blend (called "NBBZrMA"), Zr-butoxide ($Zr(OBu^t)_4$) and Metacrylic acid (MAA) are kept in stirring for five minutes. This solution is mixed together with the one of NBBs. This mixture is kept under stirring for one hour, before the addition of the photoinitiator, previously solubilized in chloroform. The molar ratios used are: $Si:Zr(OBu^t)_4:MAA= 5.5:3:6$.

The photoinitiator ((E,E,E,E,E,E)-1,13-bis-[4-(diethylamino)phenyl]-tri-deca-1,3,5,6,8,10,12-hexaen-7-one), labeled "TPP") has been synthesized through the cetolization-crotonization reaction from (E,E)-5-[4-(diethylamino)phenyl]penta-2,4-dienal and acetone in basic conditions.[24] The amount of TPP is equal to 0.2 % with respect to the numbers of acrylic groups.

### 2. 2 Deposition technique

The sol, containing 0.093 g of (Si+Zr)/liter, is kept in ultrasonic bath for 15 min to allow a good dispersion of the TPP. This solution is used to prepare films deposited by spin-coating technique at 2000 rpm for 10 sec. Samples with similar thicknesses, not much lower than one micron, are prepared. After photopolymerization, the unreacted units are efficiently developed in acetone bath for 10 seconds.

### 2.3 Characterization techniques

- The microstructure characterization of the sol-gel films is performed by FT-IR spectroscopy using a *Jasco 620* Spectrometer from 400 to 4500 $cm^{-1}$, with 2 $cm^{-1}$ resolution.

- The UV-Visible absorption spectra are collected with the spectrometer *Varian-Cary5* from 300 to 800 nm, with a resolution of 1 nm.

- The NonLinear optical characterization of the TPP in solution is performed by Two-Photon Induced Fluorescence (TPIF) technique. TPIF experiments are performed using a tunable Ti:Sapphire femtosecond laser system (*Coherent Mira 900-F*), with pulses of approximately 130 fs temporal length, 76 MHz repetition rate and 700 to 930 nm varying wavelengths. The laser beam is focused on the sample, contained in a 10 mm quartz cell, via a 40 cm focal length lens.[25] For each exciting wavelength investigated, the quadratic trend of the TPIF signal versus light intensity was verified and recorded, and the Two-photon Absorption (TPA) cross-section $\sigma_s$ was obtained using the expression:[25]

$$\sigma_s = \frac{q_s}{q_r}\frac{C_r}{C_s}\left(\frac{n_s}{n_r}\right)^2\frac{F_r}{F_s}\sigma_r \tag{1}$$

where $q_i$ are the coefficients of the quadratic fit, $n_i$ the solvent refractive indices, $F_i$ the fluorescence quantum yields, $C_i$ the concentration for the sample (suffix *s*) and the reference (suffix *r*) solutions and $\sigma_r$ is the TPA cross section of the reference. TPA cross sections of the reference chromophore (Rhodamine B in methanol) are those published by Xu et al.[26]

- The morphology of the polymerized structures, after the developing stage, is observed by Confocal microscopy (*Olympus BX51WI*), by Field Emission Scanning Electron Microscope (*FE-SEM LEO FEG Supra 35*) and by Atomic Force Microscopy (AFM, *Ntegra Mod. NT-MTD* ), in semi-contact modality.

- The two-photon polymerization experiments are performed with the same fs laser system, used also for the TPIF measurement. The excitation wavelength is fixed at 850 nm, near to the maximum of the TPA spectrum of the photoinitiator. The maximum average power measured is 650 mW. The optical set-up used is depicted in figure 1.

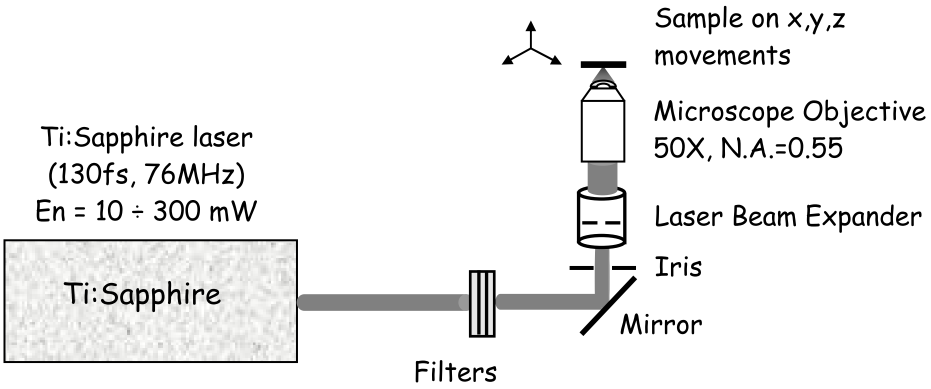

Fig. 1: Optical set-up for the two-photon polymerization experiments.

The laser beam crosses absorbing filters, allowing the control of the final optical power, and an iris diaphragm. Afterward the beam is reflected by a mirror and it is expanded by a Kepler Telescope in order to completely illuminate the entrance aperture of the focusing microscope objective (50X *Olympus LMPlan*, with a numerical aperture of 0.55 and a working distance of 6 mm). The position of the focal volume is controlled in 3D along the beam propagation, with micrometric screws. The diameter dimension of the laser beam at the focal position is estimated to be about 2 μm, considering a propagation of a Gaussian beam in the microscopic objective.

# RESULTS AND DISCUSSION

## 3.1 Optical characterization

The UV-Visible spectrum of the photoinitiator dissolved in $CHCl_3$ shows the absorption maximum centered at about 508 nm. The molecular structure and the One Photon Absorption (OPA) spectrum are reported in figure 2. Figure 2 reports also the UV-Vis spectra of the photoinitiator in NBBZrMA matrix: the inclusion of the photoinitiator into solid matrices causes a red-shift of its absorption peak, this that can be explained with interaction process with the matrix.

In order to have an efficient photopolymerization process, the photoinitiator must be able to produce radicals after excitation: these react with the double bonds of the prepolymer blend and the chain reaction starts and propagates. The characterization of the non linear optical properties of TPP is therefore an essential step to evidence the best spectral region for its excitation during the photopolymerization experiments. The TPA spectrum measured with ns regime is already reported.[27]

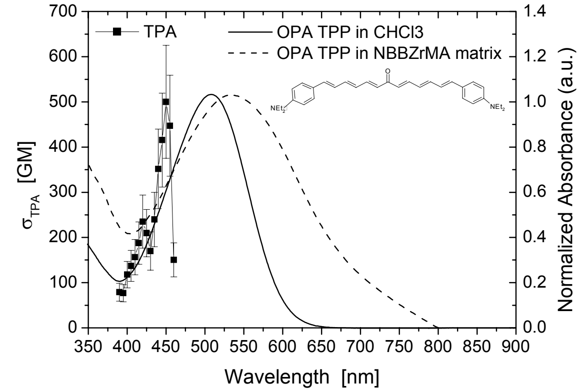

Fig. 2: One (continuum line) and two-photon absorption (dots and line) of the photoinitiator in $CHCl_3$ and OPA (dashed line) in NBBZrMA matrix. The TPP molecular structure is depicted on the inset.

Figure 2 shows the One and Two Photon Absorption spectra, measured with the previously described techniques. The wavelength abscissa scale of the TPA spectrum is halved to have a direct comparison with the linear absorption and the values of TPA cross-section are expressed in Göppert-Mayer units (1 GM = $10^{-50}$ $cm^4$ s $photon^{-1}$ $molecules^{-1}$). The maximum of TPA does not coincide with the peak of OPA, because of the symmetric structure of TPP that can induce different selection rules for the two-photon absorption.

Figure 3 shows FT-IR spectrum of the hybrid films. The almost total absence of OH groups (absorption at $3400 cm^{-1}$) confirms the high condensation level of the nanobuliding blocks. The presence of the band at about 1719 $cm^{-1}$ and 1638 $cm^{-1}$ is due to C=O and C=C bonds.

## 3.2 Two-photon polymerization

For the two-photon induced polymerization, we have chosen the wavelength at 850 nm, in order to guarantee both high TPA cross-section and high incident energies.

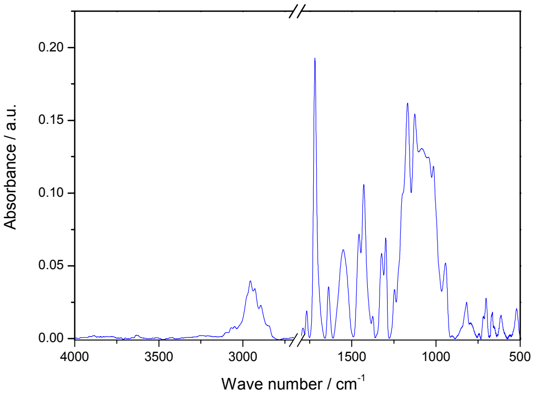

Fig. 3 : FTIR Spectrum of the hybrid film deposited on silicon substrate.

In TPIP experiments, the incident energies are varied from 5 to 50 mW and the exposure time is less than 1 sec. We have previously noted that the TPIP experiments on acrylate systems are not influenced by the presence of molecular oxygen in experimental atmosphere[12], allowing to perform the irradiations in air. Instead, the efficiency of the polymerization can be subjected to the quantity of acrylate double bounds available to the photopolymerization. For this reason, we have chosen the NBBs system with the highest number of reactive organic functions as polymerizable hybrid organic/inorganic precursor.

In this work the effect of the input energies on the final features has been investigated. Figure 4 show respectively the confocal images of the patterns remained on the substrate after the development stage. Every line represents the polymerized dots obtained with different energies, ranging 50 to 5 mW, and less than 1 second irradiation time, using a 50X microscopic objective, with N.A. 0.55. From the micrographs, it is possible to observe that the resolution on the final structure becomes more defined when the input energy decreases. In fact, it is possible to control the polymerization reactions when the energy dose is low enough to prevent diffusion of the radicals over an area larger than the laser spot.

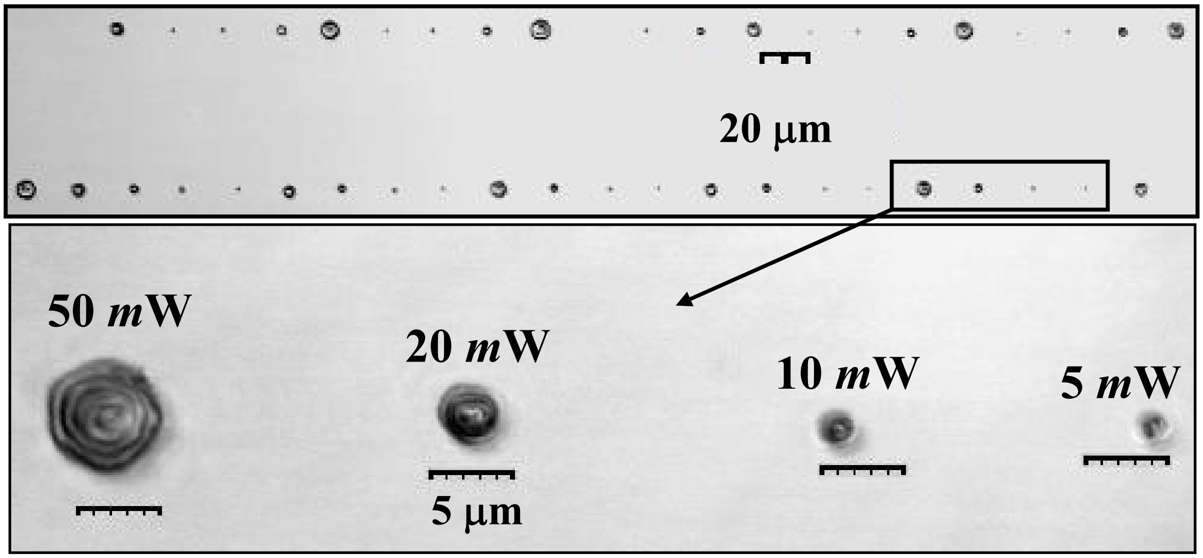

Fig. 4: Confocal images of the spots remained on the silicon substrate after the development stage. Every line represents the polymerized dots obtained with different energies, ranging from 50 to 5 mW, and less than 1 second irradiation time, with an objective 50X, with N.A. 0.55.

The estimated diameter values of the dots, at different energies, are reported, as example, in table 1. By comparing these values with the estimated dimension of the laser beam used, it is possible to confirm that only low energies allow obtaining structures with sizes comparable to the dimensions of the laser beam used.

| Incident Energies [mW] | Spot diameter NBBZrMA [µm] |
|---|---|
| 50 | 5 |
| 20 | 3 |
| 10 | 1.8 |
| 5 | 1.2 |

Table 1: Estimated diameter values of developed dots on NBBZrMA film, irradiated at 850 nm.

AFM images of different dots, reported in the previous confocal images (figure 4), are shown in figure 5 and figure 6. Figure 5 displays the 2D and 3D AFM images and the corresponding profile of a dot remained on the substrate after the development stage irradiated at 50 mW, while figure 6 show the result of the irradiation at 5 mW.

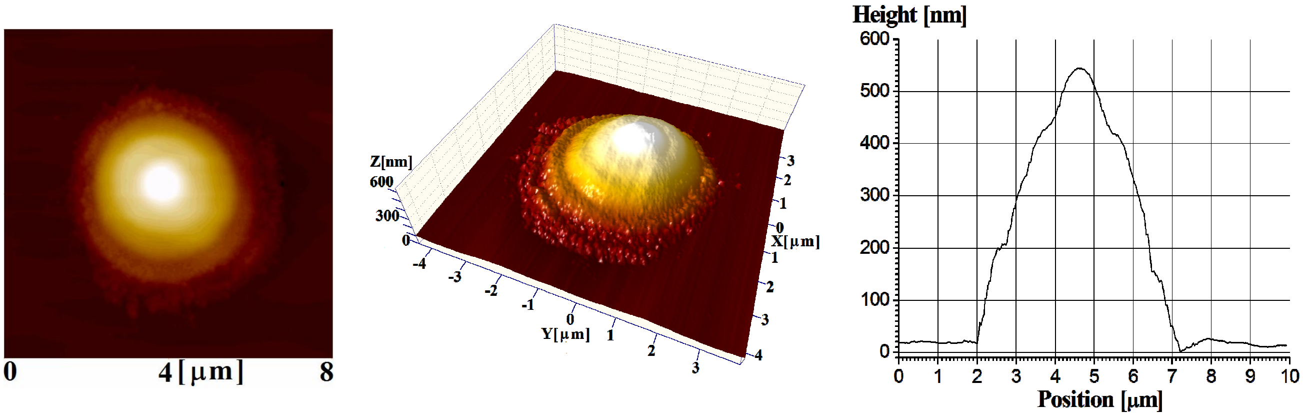

Fig. 5: AFM images and section of a spot irradiated at 50 mW remained on the silicon substrate after the development stage.

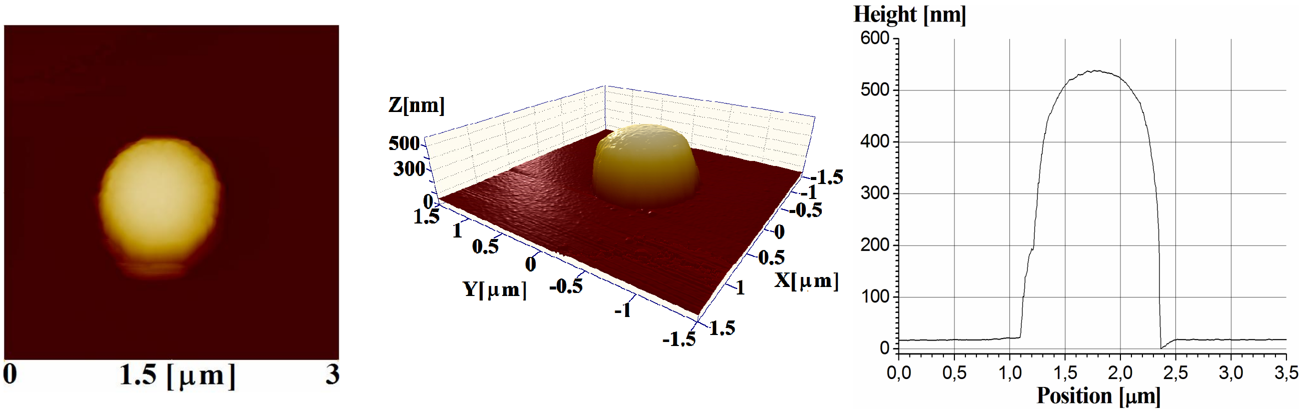

Fig. 6: AFM images and section of a spot irradiated at 5 mW remained on the silicon substrate after the development stage.

Both the spots have approximately the same height despite the different diameter, suggesting that their thickness is limited only by the depth of the film.

A different sample, realized using a 100X objective, with N.A. 0.8, has been analyzed with FE-SEM. Figure 7 shows a large area of the sample (A) with spots, photopolymerized at different input energies, ranging from 60 to 5 mW, and a magnification of two structures.

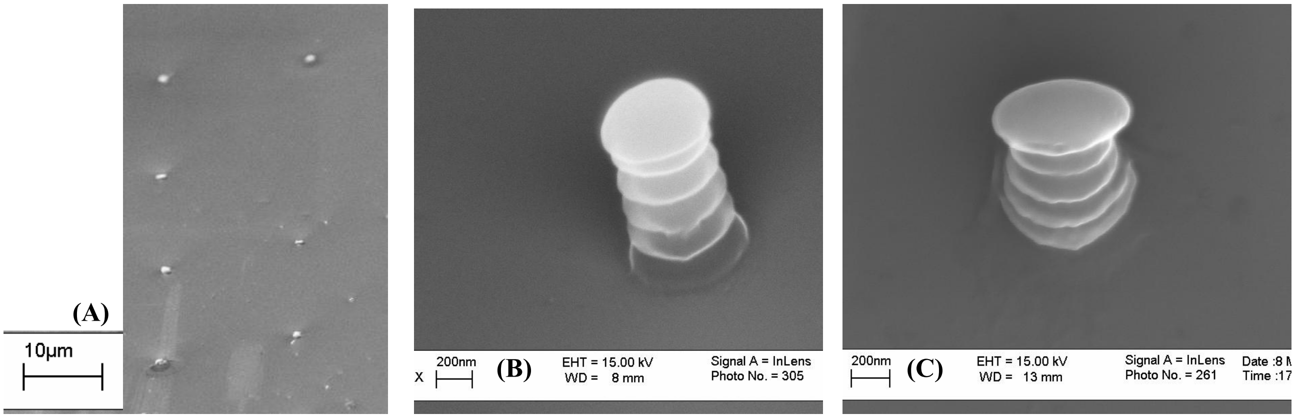

Fig.7. FE-SEM images of a photopolymerized sample, realized using energy in the range 60-5 mW and a microscopic objective 100X, with N.A. 0.8 (A) and (B, C) details of two different structures photopolymerized using 5mW irradiation energy.

Our best results have been obtained using 5 mW as irradiation energy, a high value compared with energies reported in different works. This could be due to the numerical aperture employed, the control on the exposition time, on the adhesion of the spots to the substrate and on the development conditions. Further works are in progress to increase these preliminary results. In any case this work reports for the first time a two-photon induced photopolymerization made on sol-gel materials containing Si-nanobuilding blocks.

## CONCLUSIONS

In this contribution we have reported for the first time results obtained on the photopolymerization of a new material consisting of a blend of organic-inorganic hybrid precursors, containing methacrylic functionalities, and Si-nanobuilding blocks, prepared trough sol-gel synthesis. The photopolymerization has been induced by two-photon absorption processes, activated using a novel photoinitiator.

We have tested the efficiency of the photopolymerization process by varying the incident energies and obtaining high quality results using 5mW irradiation energy. The final structures show few hundreds of nanometers sizes. The control of the excitation energy is one of the key parameter to obtain, especially when two-photon polymerization is performed, the realization of structures with small dimensions. This result that can be further improved in the aim of the fabrication of micro- and nano-patterns on sol-gel materials for 3D-photonic applications.

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# REFERENCES

1. T. Nakahama, T. Nakahama, S. Yokoyama, H. Miki and S. Mashiko, "Control of multiphoton process within diffraction limit space in polymer microstructures", *Thin Solid Films*, 499, 406-409 (2006).
2. H. B. Sun, K. Takada, M. S. Kim, K. S. Lee and S. Kawata, "Scaling laws of voxels in two-photon photopolymerization nanofabrication", *Appl. Phys. Lett.*, 83(6), 1104-1107 (2003).
3. B. Cumpston et al.,"Two-photon polymerization initiators for three dimensional optical data storage and microfabrication", *Lett. to Nature*, 398, 51-54 (1999).
4. M. Miwa, S. Juodkazis, T. Kawakami, S. Matsuo and H. Misawa, "Femtosecond two-photn stereo-lithography" *Appl. Phys. A*, 73, 561-566 (2001).
5. S. Klein, A. Barsella, H. Leblond, H. Bulou, A. Fort, C. Andraud, G. Lemercier, J. C. Mulatier, K. Dorkenoo "One-step waveguide and optical circuit writing in photopolymerizable materials processed by two-photon absorption", *Appl. Phys. Lett.*, 86, 211118 (2005).
6. W.H. Teh, U. Dürig, U. Drechsler, C. G. Smith, H. J. Güntherodt, "Effect of low numerical-aperture femtosecond two-photon absorption on (SU-8) resist for ultrahigh-aspect-ratio microstereolithography", *J. of Appl. Phys.*, 97, 054907 (2005).
7. J. Serbin, A. Ovsianikov, and B.N. Chichkov, "Fabrication of woodpile structures by two-photon polymerization and investigation of their optical properties", *Opt. Exp.*, 12, 5221 (2004).
8. A. Ovsianikov, A. Ostendorf, B.N. Chichkov, "Three-dimensional photofabrication with femtosecond lasers for applications in photonics and biomedicine", *Appl. Surf. Sci.*, 253, 6599 (2007).
9. R. Houbertz, "Laser interaction in sol–gel based materials—3-D lithography for photonic applications", *Applied Surface Science*, 247, 504–512 (2005).
10. R. Houbertz, L.Frohlich, M.Popall, U.Streppel, P.Dannberg, A.Brauer, J.Serbin, B.N. Chichkov-BN, "Inorganic-organic hybrid polymers for information technology: from planar technology to 3D nanostructures", *Adv. Eng. Mater.* 5(8), 551 (2003).
11. K. Studer, C. Decker, E. Beck and R. Schwalm, "Overcoming oxygen inhibition in UV-curing of acrylate coatings by carbon dioxide inerting, Part I-PartII", *Progress in Organic Coatings*, 48, 92-100; 101-111 (2003).
12. I. Fortunati, T. Dainese, R. Signorini, R. Bozio, V. Tagliazucca, S. Dirè, G. Lemercier, J.-C. Mulatier, C. Andraud, P. Schiavuta, J. Bottazzo, G. Della Giustina, G.Brusatin, M.Guglielmi, "Photopolymerization of hybrid organic/inorganic materials based on nanostructured molecular units for photonic applications",Proc. of SPIE, 6645, 664520 (2007).
13. P. Innocenzi and G. Brusatin, "A comparative FTIR study of thermal and photo-polymerization processes in hybrid sol–gel films", *J. of Non-Cryst. Solids*, 333, 137-142 (2004).
14. R. Houbertz, G. Domann, J. Schulz, B. Olsowski, L. Fröhlich and W. S. Kim "Impact of photoinitiators on the photopolymerization and the optical properties of inorganic-organic hybrid polymers" *Appl. Phys. Lett.*, 84(7), 1105-1107 (2004).
15. Y. Cai, J.L.P. Jessop, "Decreased oxygen inhibition in photopolymerized acrylate/epoxide hybrid polymer coatings as demonstrated by Raman spectroscopy", *Polymer*, 47, 6560-6566 (2006).
16. M. Guglielmi, G. Brusatin, G. Della Giustina "Hybrid glass-like films through sol–gel techniques", Journal of Non-Crystalline Solids, 353, 1681–1687 (2007).
17. G. Brusatin, G. Della Giustina, M. Guglielmi, M. Casalboni, P. Prosposito, S. Schutzmann and G. Roma "Direct pattern of photocurable glycidoxypropyltrimethoxysilane based sol–gel hybrid waveguides for photonic applications", *Materials Science and Engineering: C*, 27, 1022–1025 (2007).
18. G. Della Giustina, G. Brusatin, M. Guglielmi and F. Romanato **"**Direct nanopattern of hybrid sol–gel films", Materials Science and Engineering C 27, 1382–1385, (2007)
19. U. Schubert, "Organofunctional Metal Oxide Clusters as Building Blocks for Inorganic-Organic Hybrid Materials", *J. Sol-Gel Sci. Technol.* 31, 19-24, (2004).
20. P. Innocenzi, B. Lebeau, "Organic–inorganic hybrid materials for non-linear optics", *J. Mater. Chem.*, 15, 3821-3831 (2005).

21. S. Dirè, P. Egger, M.L. Di Vona, M. Trombetta and S.Licoccia, "Siloxane-Based Nanobuilding Blocks by Reaction Between Silanediol and Trifunctional Silicon Alkoxides" J. Sol-Gel Sci.Technol. 32, 57-61 (2004).
22. M.L. Di Vona, M. Trombetta, S. Dirè, P. Egger, C. D'Ottavi and S. Licoccia, " Hybrid Siloxane-Based Nano Building Blocks for Optical Applications: Optimization of the Synthetic Procedures by Spectroscopic Analysis", J. Sol-Gel Sci.Technol., 35, 151-157 (2005)
23. S. Dirè, V. Tagliazucca, G. Brusatin, J. Bottazzo, I. Fortunati, R. Signorini, T. Dainese, C. Andraud, M. Trombetta, M.L. Di Vona, S. Licoccia, "Hybrid organic/inorganic materials for photonic applications via assembling of nanostructured molecular units", J. Sol-Gel Sci. Techn., in press
24. Lemercier, C. Martineau, J.-C. Mulatier, I. Wang, O. Stéphan, P. Baldeck, C. Andraud, "Analogs of Michlers ketone for two-photon absorption initiation of polymerization in the near infrared: synthesis and photophysical properties", New J. Chem. 30, 1606-1613 (2006).
25. M. Rumi, et al.,"Structure-properties relationships for two-photon absorbing chromophores: Bis-donor diphenylene and Bis(styryl)benzene derivatives" *J. Am. Chem. Soc.*, 122, 9500 (2000).
26. C. Xu, R. M. William, W. Zipfel, and W. W. Webb, "Multiphoton excitation cross-sections of molecular fluorophores", *Bioimag.*, 4, 198 (1996).
27. C. Martineau, G. Lemercier, C. Andraud, I. Wang, M. Bouriau and P. L. Baldeck, "New initiator for two-photon absorption induced polymerization with a microlaser at 1.06 µm", *Synth. Metals*, 138, 353-356 (2003).