Invited Paper

# Hybrid Materials: a bottom-up approach for nanotechnology applications

Laura Brigo, Erika Zanchetta, Gioia Della Giustina, Giovanna Brusatin*
Industrial Engineering Department and INSTM, Via Marzolo 9, 35131 Padova, Italy

## ABSTRACT

Engineered organic-inorganic hybrid materials, HyMat, offer new opportunities for the easy, fast and cheap development of miniaturized functional devices. The integration of inorganic oxide networks, organic functional groups and optically active molecules or nanoparticles allows to obtain combinations of properties and structures otherwise impossible with traditional materials.

In particular, a simple and highly versatile synthesis platform enabling preparation of HyMat is presented, which is built up by a bottom-up sol-gel approach at low processing temperatures. A few types of key building blocks pave the way for accessing HyMat and make up their formulation, providing a means to synthesize innovative materials enabling to get:

- optically active micro and nanostructures;
- miniaturized sensors for analytes in gaseous or liquid media;
- direct patternability with a range of lithographic techniques;
- variable inorganic and organic compositions, and controlled porosity.

Examples of micro and nanostructures based on these spin-on materials with ceramic (i.e. $SiO_2$, $GeO_2$, $Al_2O_3$, $ZrO_2$, $TiO_2$,) and hybrid compositions will be presented for different applications including plasmonic or fluorescent sensors, dry-etching masks with outstanding resistance, optically active micro and nanostructured platforms and high resolution patterns.

**Keywords:** hybrid materials, sol-gel, lithography, resist, inorganic oxides, direct patterning

## 1. INTRODUCTION

Structuring surfaces by a direct lithographic process is uncommon. A functional organic or inorganic material is generally indirectly patterned, by patterning a sacrificial resist deposited on it first, and then by transferring the image of the sacrificial layer to the functional material, in a pattern-transfer step (Figure 1a). Nevertheless, this multi-step process often causes a deterioration of lithographic performance, is time-consuming, and makes the process complicated. Alternative procedures, mainly used to pattern inorganic films, attempt to simplify the traditional complex process using an organic resist pattern as a mould, depositing the film on it and then removing the organic resist by a lift-off process, leaving the patterned structures on the substrate.[1] Therefore, it is essential to broaden the spectrum of spin-on materials that behave as resists (as they proficiently interact with radiation or undergo modifications under specific thermal and pressure conditions and are further processable with development steps) but that can also be employed as final device materials (Figure 1b and c).

Organic–inorganic hybrid materials are emerging as an alternative to organic polymers for micro and nanolithography, guaranteeing both solution processability and higher lithographic performance, stability and a wider choice of properties:[3-7] thermal resistance (up to 300 °C), mechanical resistance (antiscratch), chemical endurance (resistance to dissolution). Furthermore, functional properties such as optical (i.e. refractive index), electrical, porosity, etc. can be tuned, and specific functions can be achieved by embedding nanoparticles, dyes or other active molecules, for

*giovanna.brusatin@unipd.it; phone +39-049-8275723; www.hymat.dii.unipd.it

Nanophotonic Materials XI, edited by Stefano Cabrini, Gilles Lérondel, Adam M. Schwartzberg, Taleb Mokari,
Proc. of SPIE Vol. 9161, 91610B · © 2014 SPIE · CCC code: 0277-786X/14/$18 · doi: 10.1117/12.2066677

applications in integrated devices such as fluorescent or plasmonic sensors, lasers, etc. Finally, they are built up by a simple, low-cost bottom-up sol-gel approach, typically carried out at low process temperatures (Figure 2).

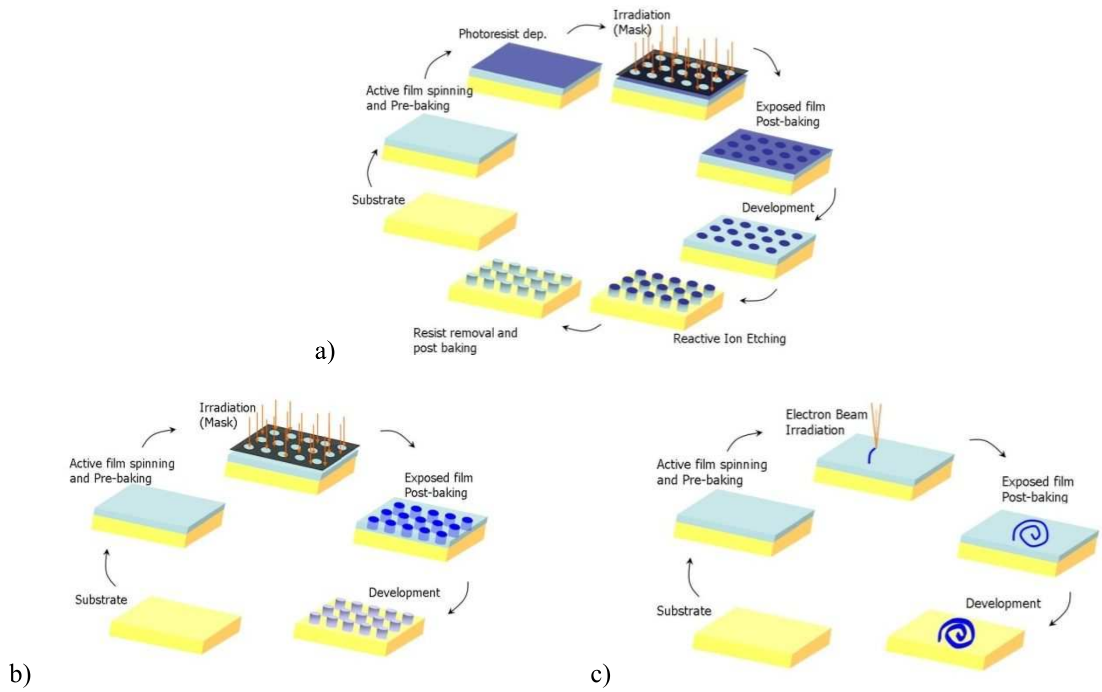



**Figure 1**: Schemes of a) conventional lithographic process and b) of direct patterning processes using X-Ray Lithography (XRL) or c) Electron Beam Lithography (EBL), from ref. 2.

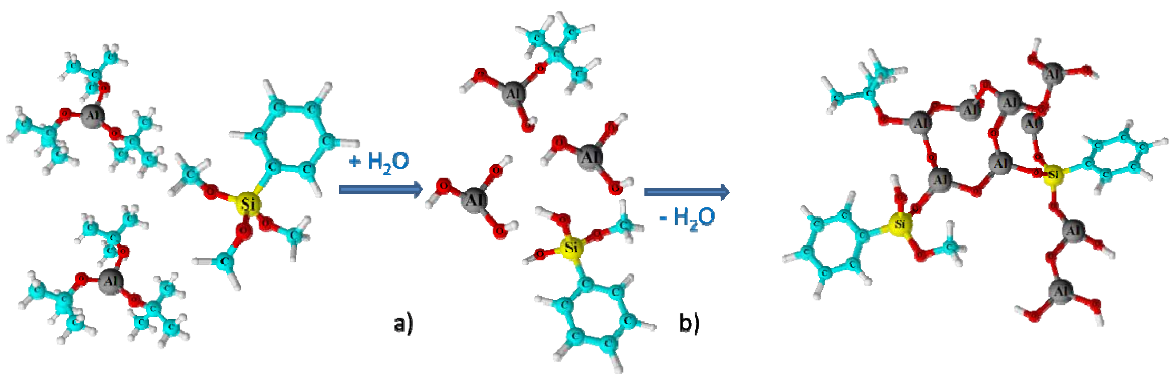



**Figure 2**: Example of a) hydrolysis and b) condensation sol-gel reactions of metal-organic precursors with formation of an organically modified partially condensed aluminum oxide network. The final represented structure is typical of a spin-coated film before lithographic processing (from ref. 8).

## 2. RESULTS AND DISCUSSION

A simple and highly versatile synthesis platform, enabling the preparation of organic–inorganic hybrid spin-on materials for micro- and nanofabrication, has been developed at HyMat Lab.[9] The engineered materials are synthesized by a bottom–up sol–gel approach.[2, 10-11] A few types of key building blocks path the way for accessing HyMat and make up their formulation: organic building blocks play the main role towards the lithographic tool, while metal alkoxides are selected for the focused applications, allowing the preparation of thermal, pressure and radiation sensitive resists in a wide range of ceramic compositions ($GeO_2$, $TiO_2$, $ZrO_2$, $HfO_2$, $Al_2O_3$, PZT,…) coupled with organic functionalities (epoxy, acrylate, phenyl, …), with a high degree of control over composition, structure and processability.

The main building blocks that define a HyMat resist structure are:

- metal organic precursors: in the periodic table of Figure 3a, metals (Me) whose alkoxides are commercially available or studied are shown. Their function is to confer optical, mechanical or other functional properties to the patterned films, depending on their nature and concentration;
- organically modified silicon alkoxides, whose organic function is polymerizable (Figure 3b). They allow to obtain high optical quality glassy hybrid patterns hardened by organic polymerization;
- organically modified silicon alkoxides whose organic function acts as network modifier (Figure 3c), or as bridging group and functional species at the same time. They can be used for patterning by radiation-assisted lithography to produce completely inorganic patterned structures;
- organic monomers whose role is to tailor the rheology of the film during the imprinting process and contribute to harden the pattern thermally or by radiation (Figure 3d);
- organic molecules used for patterning by photodegradation to produce completely inorganic patterned structures (Figure 3e).

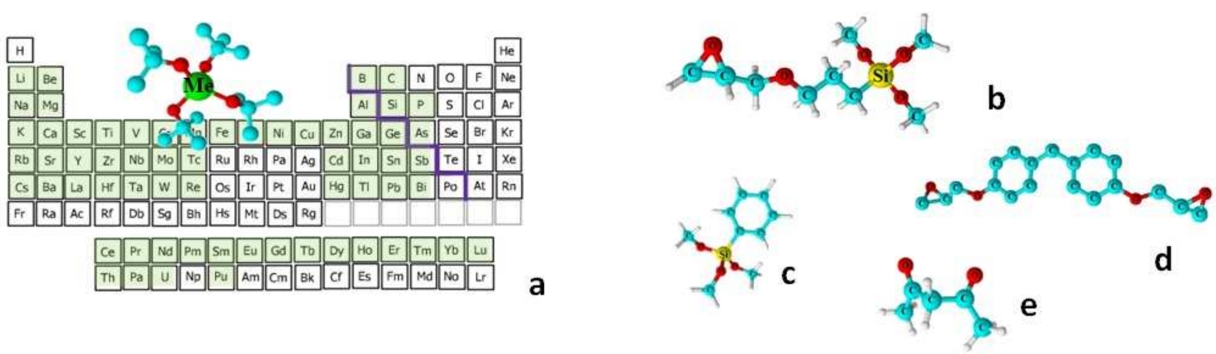



**Figure 3**: Main building blocks that define the HyMat resist structure: a) metal organic precursors, examples of organically modified silicon alkoxide with b) organic polymerizable function or c) organic modifier function, d) example of organic monomer and e) organic molecules added to pattern the film by photopolymerization or photodegradation.

In the following sections, few examples on the performances of HyMat are reported, showing how these materials are prepared in formulations allowing their use as functional resists, to produce in one step micro and nanopatterned features for specific applications.

### 2.1 Positive and negative tone microporous HyMat: high resolution direct patterns and sensing applications

Natively microporous photoprocessable sol-gel systems, exhibiting a positive or negative tone, have been synthesized starting from a bridged silsesquioxane precursor, 1,4-bis(triethoxysilyl)benzene. The material structure consists of a silica inorganic network built up around an organic moiety, an aryl bridge, through hydrolysis and condensation reactions of the precursor alkoxydic groups.[11-13] This material has been demonstrated to behave as a high resolution resist for electron beam lithography (EBL), as reported in ref. 14. Dense patterns down to 25 nm half-pitch and isolated structures down to 30 nm were demonstrated, exploiting the positive tone, and dense patterns down to 60 nm half-pitch were obtained in the negative tone. Etching selectivity in fluorinated gases for phenyl-bridged polysilsesquioxane (ph-PSQ) nanostructures on silicon substrates is 1:9 for the positive tone and 1:12 for the negative tone. Figure 4 shows variable resolution patterns of isolated lines, dense lines and spaces, and arrays of holes written into positive tone films; also negative tone high resolution structures have been demonstrate in ref. 14.

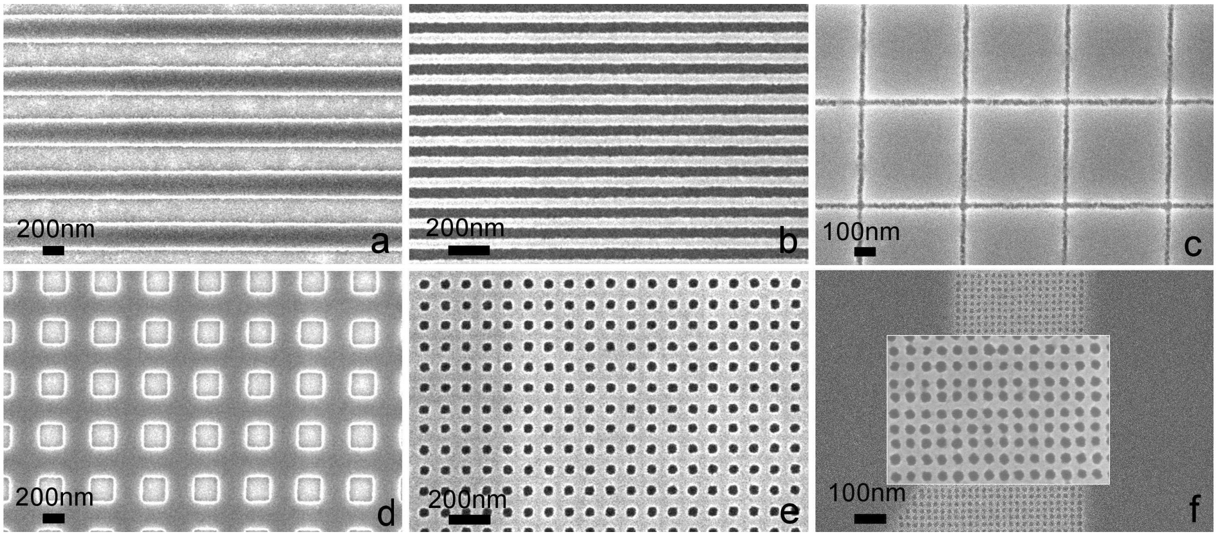



**Figure 4**: SEM images of dense lines, dots and isolated lines in 60 nm thick positive tone ph-PSQ films, fabricated applying either a PEB at 500°C for 2 min or a PEB at 300°C for 120 min: a) 250 nm and b) 50 nm half-pitch lines; c) 30 nm isolated lines; d) 250 nm and e) 50 nm half-pitch holes; f) 25 nm half-pitch holes (from ref. 14).

Exploiting the positive tone of this directly patternable HyMat, its natively porosity, the functionalizability by incorporating active species or properly designing the organic component of the hybrid network, ph-PSQ micro and nanostructures were used to realize microsensors in a single-step process.[15]

Figure 5 shows micropatterns fabricated on ph-PSQ films by X-Ray Lithography (XRL). The exposure to X rays leads to a progressive alkyl and aromatic compound elimination and promotes inorganic condensation in the system. By doping the HyMat with a covalently linked methoxyquinolinium dye,[16] sensing films patternable by pholithography are obtained, allowing to produce optical microdevices, where fluorescence properties are achieved directly on the patterned coatings.

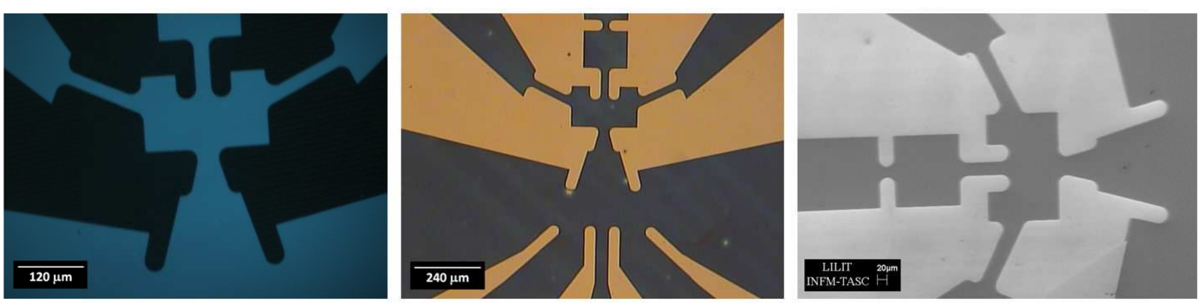



**Figure 5**: Fluorescence (left), optical (center) and scanning electron (right) microscope images of a micropattern created by XRL on a thin film prepared from a ph-PSQ matrix doped with a covalently linked quinolinium derivative (from ref. 15).

A different type of optical sensor was realized by exploiting the presence of the organic group incorporated into the hybrid network of ph-PSQ, the benzene ring, which interacts through an affinity binding, $\pi$–$\pi$ stacking,[17] with aromatic hydrocarbons. Figure 6 shows nanostructured plasmonic sensors fabricated as sinusoidal surface plasmon metallic gratings embedded in the same functional and porous hybrid sol–gel material based on ph-PSQ. The metal layer is in contact with the environment through the sol-gel film, which works as sensitive element, changing its dielectric properties upon interaction with aromatic hydrocarbons. The combination of sensitivity, transparency and patternability offered by ph-PSQs gives the exceptional possibility to fabricate innovative optical sensors with straightforward processes.[18]

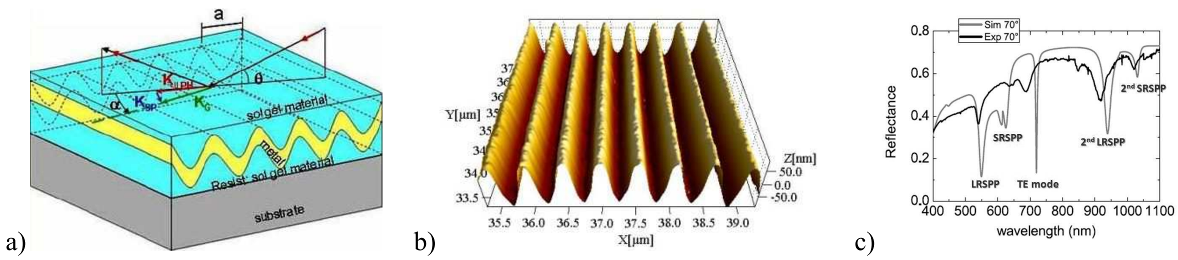



**Figure 6**: a) Sketch of the multilayer structure of a SPG embedded in a functional and porous sol–gel material, ph-PSQ. b) 3D AFM recording of a ph-PSQ film, soft-imprinted using a PDMS replica of a sinusoidal master. c) Experimental and simulated reflectance spectra, of a SPG embedded in ph-PSQ films. They were acquired at 60° azimuth with a 150° polarization angle for the incident light. The set of plasmonic dips, for increasing wavelength, were identified as long range and short range surface plasmon polaritons (LRSPP and SRSPP respectively), TE mode, and the second LRSPP and SRSPP resonances (from ref. 18).

## 2.2 Spin-on HyMat for electron- or photon-based lithography with outstanding resistance to dry etching

The need for directly patternable spin-on hard masks that already possess the proper dry etching resistance with respect to silicon is increasing. The reported HyMat resist combines the exceptional properties of alumina as an etching mask with the ease of deposition and patterning processes typical of organic resists, with the further advantage of being patternable by EBL,[8] XRL,[19] UV Lithography (UVL) and Nano Imprint Lithography (NIL). The resist solution is synthesized by the sol-gel method starting from aluminum butoxide and trimethoxyphenylsilane precursors (Figure 2). Figure 7 shows SEM images of the developed resist (a) and of the etched silicon structures obtained using alumina patterns produced by the EBL (b) and XRL (c) as etching masks. The zoomed image of the etched pattern shows the achievable sidewalls verticality and smoothness. Structures with sub-micrometer resolution features were etched down to a depth of 3 μm, with only 30 nm thick resist masks, resulting in a selectivity of 100:1, similar to that of metallic masks.

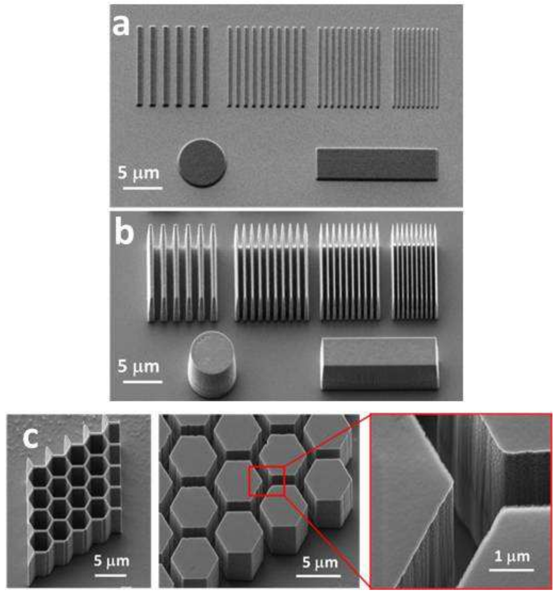
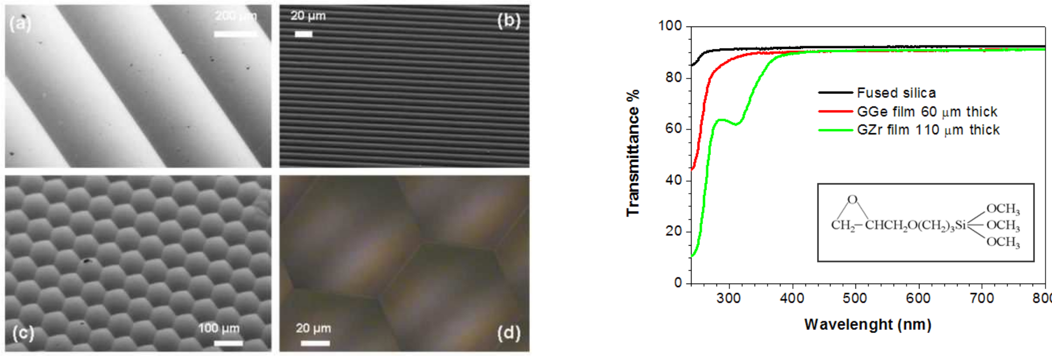



**Figure 7**: SEM images of the developed resist (a) and of the etched silicon structures obtained using the EB (b) and X-Rays (c) alumina patterns as etching masks (from ref. 8).

### 2.3 Organic-inorganic hybrid patterned structures based on spin-on epoxy systems

HyMat systems synthesized starting from 3-glycidoxypropyltrimethoxysilane (GPTMS, inset of Figure 8e) with the addition of different inorganic oxide precursors, in particular Si tetramethoxide (TMOS), Ge tetraethoxide (TEOG), Zr butoxide (ZrBut) and Ti propoxide (TiProp) for $SiO_2$, $GeO_2$, $ZrO_2$ and $TiO_2$ based films have been developed.[2, 20-22] Although hybrid systems based on $GeO_2$, $ZrO_2$ and $TiO_2$ and acrylate as polymerizable functionalities are probably the most studied photopatternable materials for direct fabrication of micro-optical elements and optical waveguides, the use of films bearing epoxy functionality as directly patternable materials is rarely investigated. Moreover, the few studies present in literature are focused on lithographies using UV light, while direct micro and nano patterning by EBL,[14, 23, 24] XRL[2, 13, 25] and NIL[26-28] is less frequently reported.

Examples of engineered epoxy based hybrid for the fabrication of microlens arrays were reported in ref. 29. The investigated sol–gel systems exhibit enhanced transparency in the near UV region with respect to most commercial thermoplastic polymers and sol–gel materials; in addition, they offer a better shape stability and superior mechanical properties, such as higher elastic modulus and hardness, improving the perspectives of the introduction of microstructured and nanostructured surfaces in applications where resistance to environmental mechanical–chemical degradation mechanisms is highly desirable. Figure 8 shows SEM images of cylindrical microlenses with 400 (a) and 10 µm (b) of period. Triangular array of spherical lenses with 80 µm of period imaged by SEM (c) and optical microscopy (d). The UV-Vis transmittance spectra of GPTMS based hybrid sol–gel materials is reported in Figure 8e, showing high transparency in the UV region of epoxy based systems respect to acrylate.




(e)

**Figure 8**: (a) SEM images of cylindrical microlenses with 400 (a) and 10 lm (b) of period. Triangular array of spherical lenses with 80 μm of period imaged by SEM (c) and optical microscopy (d). (e) UV–Vis transmittance spectra of GPTMS based hybrids (from ref. 29).

Another example of patterned structure based on GPTMS is the GPTMS-$GeO_2$ system; it was realized to have a controlled refractive index of 1.48 and successfully patterned by thermal nanoimprinting with precise geometrical parameters.[30] The 1D periodic structures realized with a silicon master having a period of 406 nm and features depth of 200 nm are shown in Figure 9d and c, and were used to realize a Distributed Feedback (DFB) laser (Figure 9a). The deposition of an active sol–gel layer, doped with quantum dots, on such grating allowed to obtain a lasing emission around 620 nm. The obtained samples show a uniform pattern over a large area of about 2 cm × 2 cm with a 400 nm period and features depth of 200 nm. To transform the Bragg grating to a prototype laser, a quantum dot (QD) doped zirconia matrix was simply deposited on top of the corrugated surface.

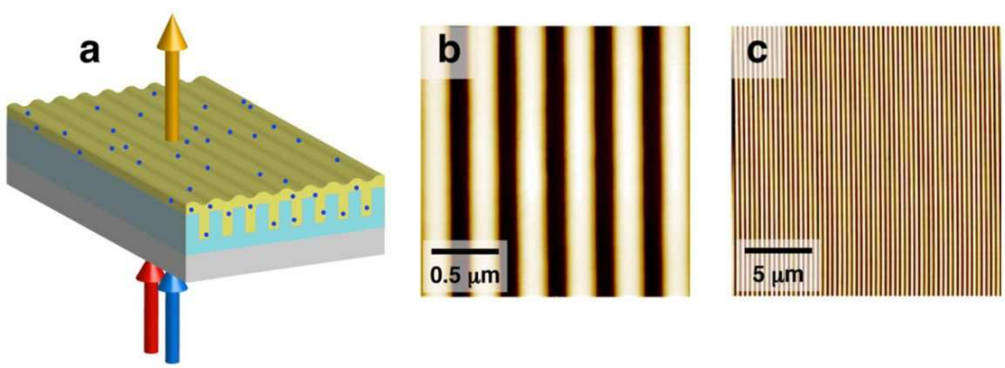



**Figure 9**: a) Pumping geometry for lasing characterizations. b) AFM measurement of 20×20 $\mu m^2$ of DFB grating, showing the large area uniformity of the structure. c) AFM measurement of 2 μm × 2 μm to check the quality of DFB grating (from ref. 30).

Lasing characteristics of the device were investigated following optical pumping by one- and two-photon excitation (Figure 9a). Initial investigations of a 158 nm thick QD/$ZrO_2$ film on DFB presented lasing peaks at 627 and 635 nm for one- and two-photon pumping, respectively (Figure 10a and c). At low fluencies only the spontaneous emission was detectable, however by increasing the input energy above the lasing thresholds (Figure 10b and d), true laser emission was observed.

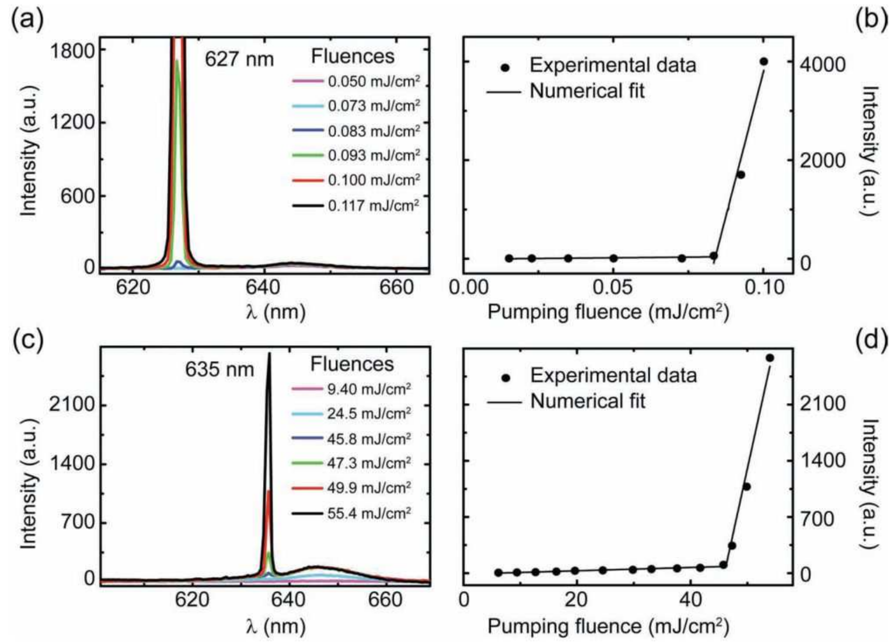



**Figure 10**: Emission of the 150 nm thick prototype at increasing fluences pumped at 400 (a) and 800 nm (c) with relative peak intensity (b,d). The lasing peak appears above thresholds of 0.083 mJ $cm^{-2}$ (b) and 47.8 mJ $cm^{-2}$ (d) for one- and two-photon pumping, respectively (from ref. 30).

## 3. CONCLUSIONS

Advanced resist materials are essential to the outcome and performance of the main lithographic tools and strategically relevant for the addressed nanotechnology applications. A highly versatile synthesis platform enabling preparation of HyMat, new spin-on resists built up by a bottom-up sol–gel approach for a direct patterning process, has been presented.

A few types of key building blocks enable the engineering and constitute the formulation of HyMat: organic moieties play the main role towards the lithographic tool, while metal alkoxides or further specific molecules are selected for the addressed applications, allowing thermal, pressure and radiation sensitive resists in a wide range of ceramic compositions coupled with organic functionalities, with a high degree of control over composition, structure and processability.

The amount and type of these building blocks determine the key points of HyMat success: (1) direct patternability with different lithographic tools with high performance; (2) presence of both positive and negative tones, exploited thanks to a deep knowledge and control over material interactions with radiation or thermal/pressure-driven processes and developers, that contributes to reduce costs and steps of a lithographic process; (3) variety of compositions, from both organic-inorganic hybrid to totally inorganic, and chemical-physical properties as transparency, refractive index, stiffness, porosity, sensing functionality, offering a broad field of possible applications for HyMat as final device material.

The one-step development of sensing devices, high resolution patterns, dry-etching masks with outstanding resistance, optically active micro and nanostructures has been described.

## ACKNOWLEDGEMENTS

Fondazione Cariplo is greatly acknowledged for the financial support through the project no. 2012-0186.

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