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Interferential lithography of Bragg gratings on hybrid organic–inorganic sol–gel materials

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ABSTRACT

In this work we report on the application of laser interference lithography (LIL) to create periodic features on a photosensitive hybrid organic inorganic (HOI) sol–gel material based on 3-glycidoxypropyltrimethoxysilane (GPTMS).

To better understand the mechanisms behind the grating formation and optimize the overall process, the chemical changes produced by the laser exposure have been investigated by FTIR spectroscopy. The effects of the development step on the hybrid sol–gel network have been also discussed, trying to explain the origin of the selective dissolution of the unexposed area.

High quality gratings with lines down to 250 nm have been realized by LIL, in the Lloyd's mirror configuration, and their morphological characterization has been performed by AFM and SEM.

The generation of profiles with controlled sinusoidal features on HOI sol–gel materials could be exploited in different applications such as the realization of plasmonic crystals for sensing applications or as master molds for nanoimprinting lithography.

1. Introduction

A strategic issue in several research fields is the developing of innovative materials. Especially in optical applications, many efforts have been made in the domain of photosensitive systems and their use in micro and nano fabrication lithographic techniques as the final material of the device.

In particular, HOI sol–gel systems are challenging materials since they are able to join some of the glass assets with their lithographic processability. They are becoming a key topic due to the low cost and ease of fabrication process, good optical and mechanical properties and the outstanding potentiality to be directly patterned by several technologies. The organically modified precursors used for the synthesis can contain polymerizable groups in their structure, such as double bonds and epoxy rings. This peculiarity has been already exploited for direct patterning of sol–gel films in a "one step" process by different lithographic techniques (such as UV, X-ray and electron beam lithography) [1–3] and could have great benefits for cost effective mass production.

HOI materials can be used in combination with laser interference lithography (LIL), an emerging and promising technology for the realization of large area 1D and 2D periodic structures on photosensitive materials [4,5]. The spatial-period of the features can be easily tuned, and can be as low as half of the interfering light wavelength, according to the Bragg's law. This technique allows the fabrication of structures of the order of 100 nm from UV wavelengths. The two-beam-interference method represents a fundamental technique for the fabrication of Bragg gratings, complementary to more expensive and time consuming processes such as electron beam lithography (EBL) or high throughput and large area nanoimprinting technologies which often require costly and breakable master stamps.

Periodic structures or Bragg gratings find applications in many important photonic and optical devices such as light trapping systems for photovoltaic panel [6], distributed feedback (DFB) lasers [7], photonic crystals [8], optical data storage [9] and plasmonic crystal for biosensing [10].

Therefore, the combination of LIL with suitable sol–gel photosensitive materials and with EBL for mix and match lithographic processes can introduce interesting advantages in several application fields. The presence of inorganic network significantly improves many important properties compared to the polymers, such as rigidity, environmental and chemical resistance and dimensional stability of the patterned features. Recently, HOI sol–gel systems have been employed [7,11–14] in laser based

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lithographic techniques, but the more investigated HOI sol–gel materials are the acrylic ones, frequently mixed with titanium [12,13] or zirconium oxides [7,14].

In this work we describe the fabrication of 1D periodic structures by laser interference lithography (LIL) on a photosensitive epoxy HOI sol–gel material based on 3-glycidoxypropyltrimethoxysilane (GPTMS). A photoacid generator has been added to the solution in order to initiate the cationic photopolymerization of the epoxy rings upon exposure to UV light. Epoxy HOI sol–gel systems have the advantage to exhibit low shrinkage during the photopolymerization process, useful for the improvement of the spatial resolution and the dimensional stability. Moreover, in comparison with the acrylic materials, the cationic polymerization mechanism is not inhibited by the presence of oxygen and cannot be started only by the temperature as in the case of radical processes. These features allow to obtain a better control of the polymerization reactions of the epoxy groups. The influence of laser exposure and the developing step on the film structure has been investigated to have a better insight of the processes controlling the gratings generation. Sinusoidal features with different periods and surface modulation depth have been presented.

2. Experimental details

The current system proceeds from a previous one which has been extensively investigated as a photo-structurable material by means of different lithographic techniques [3,15]; in this work the synthesis protocol has been modified to further improve the film optical quality. The solution has been prepared starting from 3-glycidoxypropyltrimethoxysilane (GPTMS), one of the main sol–gel precursors used to synthesize epoxy based HOI materials. GPTMS possesses an organic chain ending with an epoxy ring: the presence of this functionality, linked to the inorganic network, enables this system to be a photosensitive material.

A metal alkoxide, germanium tetraethoxyde (TEOG), has been reacted together with GPTMS, and the proper synthesis conditions have been selected to preserve the photopolymerizable epoxy groups inside the final film structure, in spite of the presence of this Lewis acid. GPTMS has been hydrolysed with a 0.5% molar concentration of HCl (1N) for 1 h at room temperature. TEOG has been added to the solution with a molar ratio GPTMS:TEOG = 80:20 and the sol has been left to react under reflux for 1 h 30 min. The final sol concentration has been set between 60 and 150 g/l (SiO_2 + GeO_2). The solution has been filtered by a microporous membrane (0.2 μm Millipore). HOI films, with the desired thickness, have been deposited by spin coating technique on silicon wafer (100) and all the samples have been thermal treated on a hot plate at 80 °C for 15 min in order to remove the residual solvent (pre-baking). As can be seen in Fig. 1, a wide interval of thicknesses can be obtained, ranging from some microns to few hundred of nanometers. This gives the possibility to fit the requirements of a great number of applications.

To promote the cationic polymerization of epoxy groups under UV/laser exposure, a commercial photoinitiator has been added to the solution with a molar concentration of 1% with respect to GPTMS. 4-(Phenylthiophenyl)diphenylsulfoniumtriflate (DPST, Aldrich) belongs to the photoacid generator (PAG) class and has the main absorption peak around 300 nm. The UV–Visible absorption spectrum of this compound, dissolved in methanol, is depicted in Fig. 2 and its chemical structure is shown in the inset.

Different Bragg gratings have been realized by means of LIL technique with a Lloyd's mirror setup: a rotational stage can be oriented in order to select the interference period of the exposed gratings. Sinusoidal features with different geometries and optical parameters have been presented and an IL exposure dose-developing time study has been performed to control the oscillation amplitude and the surface roughness.

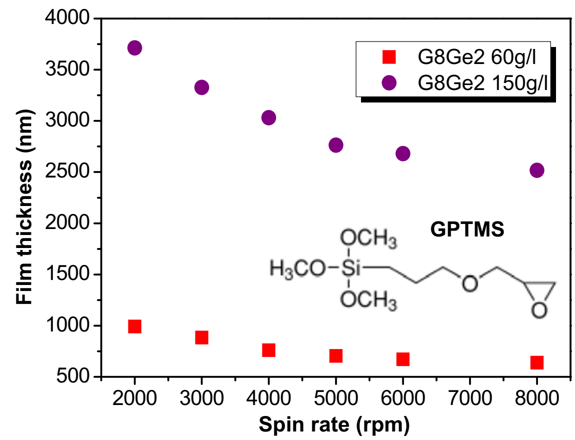

Fig. 1. Film thickness in function of spin rate. The inset shows the chemical structure of GPTMS, the main precursor of the HOI sol–gel system.

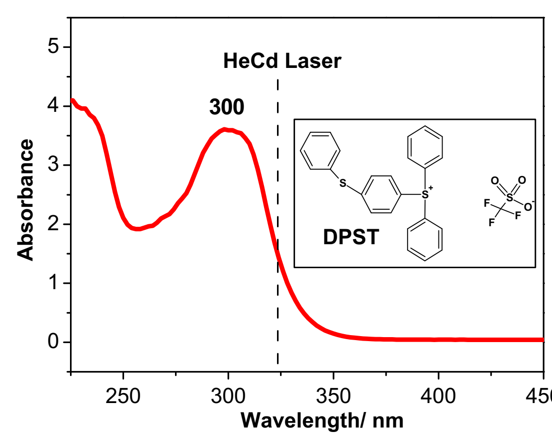

Fig. 2. UV–Vis absorption spectrum of DPST in methanol. The dash line indicates the emission of the HeCd laser used for LIL exposures. In the inset, the chemical structure of DPST is reported.

Exploiting the two-beam interference excitation of a 50 mW HeCd laser (λ = 325 nm, KIMMON Koha-Model IK3501R-G), a sinusoidal light intensity pattern has been generated and a periodic modification has been induced on the UV-sensitive sol–gel films. The period can be easily and continuously varied from many microns down to ~170 nm. A post-exposure bake at 60 °C has been applied to all samples for 60 s and grating structures have been obtained dissolving the unexposed regions by means of a diluted NaOH solution (NaOH: H_2O = 1:100) for 5–15 s, and then rinsing in water before drying with nitrogen.

The effects of UV laser exposure on the films have been analyzed by Infrared Spectroscopy; infrared absorption spectra have been recorded in the range of 400–4500 cm^{-1} by a Fourier Transform Infrared spectrometer (Jasco FT-IR-620), with a resolution of ±4 cm^{-1}.

Finally, the quality of the gratings has been characterized by atomic force microscopy (AFM) in order to detect pattern deformation or other defects and to evaluate the period and depth of the features achieved using different process conditions. The AFM images have been taken by means of a VEECO multiprobe in air tapping mode, with non-conductive Si tips, located at CNR-TASC National Laboratory (Trieste). SEM images have been also presented.

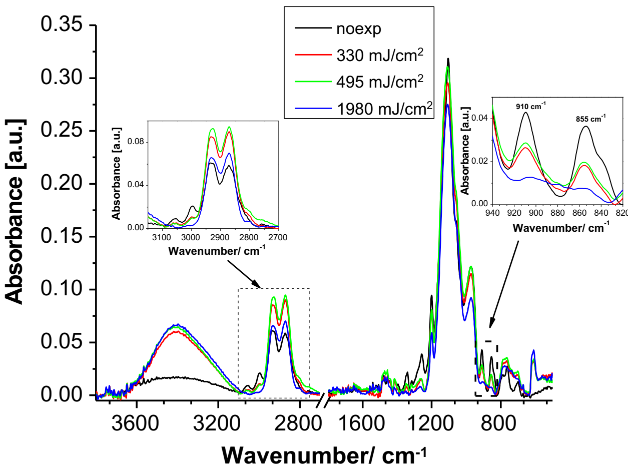

Fig. 3. FTIR absorption spectrum of hybrid sol–gel film exposed to increasing dose. In the insets, the characteristic absorption bands of the epoxy group are reported.

3. Results and discussion

To realize good quality periodic structures by LIL technique, the main issue is the correct transfer of the intensity pattern into the photosensitive material. The response to UV light of a similar GPTMS based sol–gel system has been already investigated using a common XeHg lamp, with emission of lines in a broad spectral range (280–400 nm) [2,15]. Anyway, it's of primary importance to explore the effects of UV exposure on the hybrid film, by means of a HeCd laser peaked at 325 nm. To fit the laser wavelength, the right cationic photoinitiator has to be selected. DPST presents an absorption peak centered at 300 nm and Fig. 2 shows as the laser line falls in a region where the initiator still absorbs enough.

The evolution of the HOI structure as a function of the UV exposition dose has been evaluated on planar films by FTIR spectroscopy (Fig. 3). The exposure has been carried out with a laser intensity of about 550 $\mu W/cm^2$ on the sample surface, and the doses reported in Fig. 3 correspond to irradiation time of 10, 15 and 60 min, respectively. The FT-IR spectra show how the laser irradiation of the samples reduces the signals around 3060–3000 cm^{-1} and 910 cm^{-1}, characteristic of the epoxy rings [3]. The decreasing of these absorption peaks indicates that the ring opening reaction has been initiated, and the photopolymerization process seems to occur in a similar fashion to the exposure with an high pressure XeHg lamp. The organic crosslinking induced by the UV laser exposure leads to an hardening of the structure and decreases the solubility of the exposed areas in organic or basic solvents (negative tone behavior). Even if the epoxy signals completely disappear only at the highest dose, the formation of the three-dimensional network reaches a sufficient degree of polymerization just after 10 min of irradiation, becoming insoluble in diluted NaOH. Anyway, an important difference can be noted respect to the use of other light sources such as X-rays and UV [1,2]: the exposure with the HeCd laser does not produce any degradation of the film structure even after 1 h, as evidenced by the absence of the peak at 1725 cm^{-1} [2,3]. This indicates a better efficiency of laser polymerization of epoxy rings, without unwanted secondary effects. In fact, the appearance of the absorption band around 1725 cm^{-1} can be explained by the formation of C=O bonds, probably due to the breaking of the etheric group in the propylic chain of GPTMS.

The optimization of exposure dose plays an essential role in the quality of the final structures, but the morphology of the sinusoidal gratings has been influenced by other several experimental conditions. The development step is a key point in the pattern generation and many parameters, such as the pre and post-exposure thermal treatments (time, temperature) and the solvent/time used to remove the unexposed areas have to be carefully selected to obtain good relief profiles.

Exposure time has been set around 10 min (laser intensity of 550 $\mu W/cm^2$) and it has been optimized according to the grating periodicity. The dose has been adjusted to minimize the proximity effect for smaller grating, applying shorter exposure time. The dark fringes are not completely dark and higher irradiation time has been verified to decrease the depth of the sinusoidal profile. After the exposition, a post-baking of 1 min at 60 °C has been applied and the film has been developed in diluted NaOH for different times (5 s, 10 s and 15 s). The height of the structures reaches a maximum at 10 s, after that time the developer probably starts to etch also the exposed areas and a profile roughness appears.

Fig. 4 shows the AFM images of the gratings with two different periods, 500 nm and 1 µm. The patterns look homogenous and the sinusoidal relief is perfectly symmetric. Anyway, the smaller

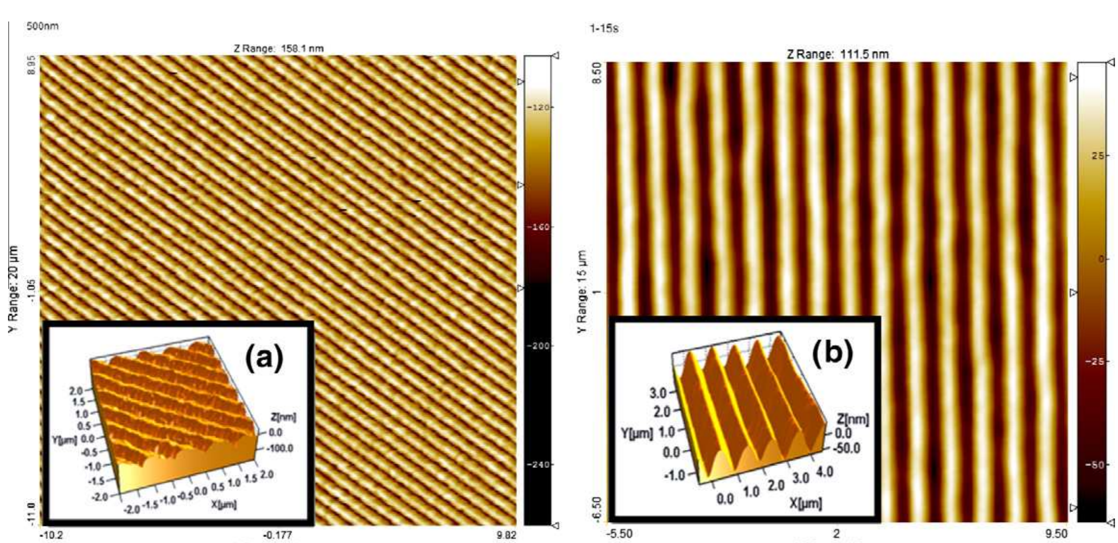

Fig. 4. AFM images of diffraction gratings with periods of 500 nm, field size 20 × 20 μm^2 (a) and 1 µm, field size 15 × 15 μm^2 (b) fabricated with the two-beam interference system. In the inset the 3D images of zoomed scans of the patterns are shown.

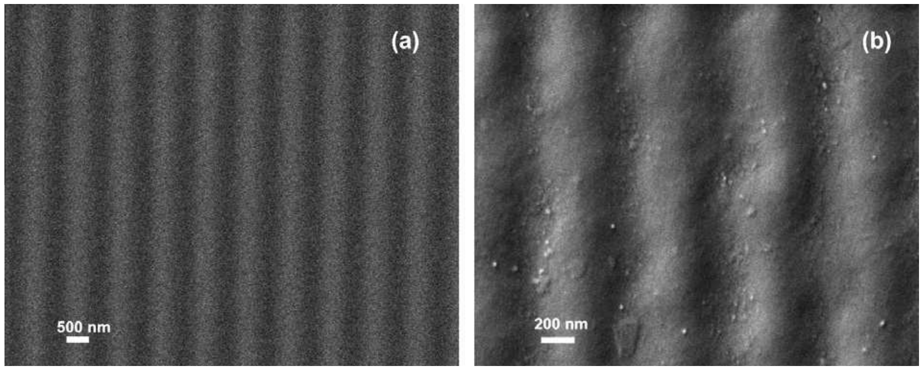

Fig. 5. SEM images of modulation patterns with periods of 1 μm (a) and 650 nm (b) realized by LIL.

grating has a lower depth (around 40 nm) than the 1 μm structures (100 nm) and an evident line roughness. The same remarks can be made observing the SEM images, reported in Fig. 5. In spite of their low contrast due to the non-conductive sample surface, the line irregularity of the smaller grating (650 nm period) appears clearly respect to the 1 μm modulation pattern.

The generation of profiles with controlled sinusoidal features on hybrid sol gel materials will be exploited in the realization of plasmonic crystals for sensing applications [9], by depositing a metallic coating directly on the hybrid gratings. The advantage of using HOI sol–gel materials in the realization of plasmonic crystals is the control of both optical and geometrical parameters (period and amplitude) in order to match the optimal coupling condition for surface plasmon polariton (SPP) propagation. Alternatively, the same periodic relief patterns could be also exploited as master itself, thanks to its higher rigidity respect to usual polymeric resists or in the replica moulding technique. This allows to realize plasmonic crystals in a wider range of alternative HOI or polymeric materials, other than the photosensitive ones, whose optical and functional properties are tunable according to the specific device needs.

4. Conclusions

In this work we have shown as an epoxy sol–gel system can be successfully exploited as a recording material in the LIL technique. Bragg gratings with period ranging from 1 μm to 500 nm have been achieved: patterns appear homogeneous on a large area and the relief profile is symmetric and perfectly sinusoidal. The results point out as the present photosensitive hybrid sol–gel material could be a versatile and an attractive candidate in the realization of many optical devices such as plasmonic crystal. The tuning of the refractive index, simply by changing the molar ratio of the organic and inorganic part and the easy doping typical of HOI materials represent an important chance to expand the field of application.

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