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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.

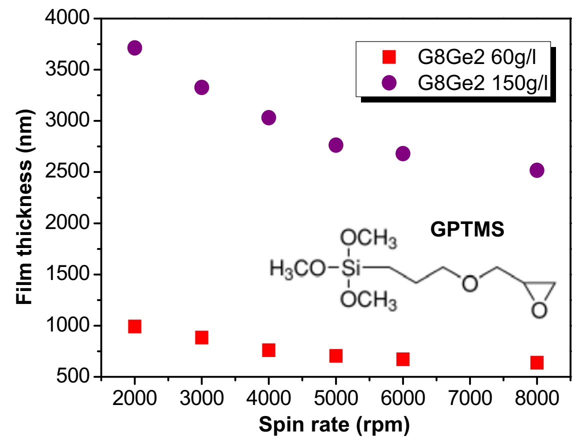

Fig. 1. Film thickness in function of spin rate. The inset shows the chemical structure of GPTMS, the main precursor of the HOI sol–gel system.

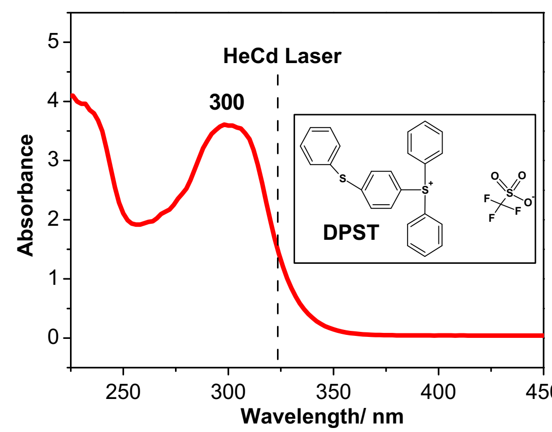

Fig. 2. UV–Vis absorption spectrum of DPST in methanol. The dash line indicates the emission of the HeCd laser used for LIL exposures. In the inset, the chemical structure of DPST is reported.

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.