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# Direct laser writing of microoptical structures using a Ge-containing hybrid material

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**Abstract**

We present our investigations into the direct laser writing of a novel germanium-containing hybrid sol–gel photosensitive material for optical applications at micro scale. We employ this material in the fabrication of photonic micro-structures, such as aspheric lenses and prisms; these are well-shaped and provided good optical performance. The material exhibits good transparency and structurability, and three-dimensional structures with sub-100 nm resolution are achieved. We demonstrate the suitability of the direct laser writing method for the rapid production of custom shaped microoptical components. Since germanium glasses are widely used in fiber optics, the combination of direct laser writing with this specially designed, functional material opens an interesting way in fabricating structures for controlling light flow.


*Keywords:* Laser *3D* nanofabrication; Microoptics; Polymerization; Multifunctional devices; Fiber optics; Hybrid materials; Integrated systems; Germanium

## 1. Introduction

Micro/nanofabrication based on multiphoton polymerization direct laser writing (*DLW*) is attracting a lot of attention as it possesses the intrinsic ability to fabricate three-dimensional (*3D*) structures such as photonic crystals (*PhC*), plasmonic and metamaterial components, voids or channels, and many other components with complicated geometry. The technology is based on simultaneous multiphoton absorption; when the beam of an ultrafast pulsed laser is tightly focused into a photopolymerizable material, it can initiate photomodification only within the focus. By moving the laser focal point, *3D* micro/nanostructures can be directly written in the photopolymer [1,2]. To date, several commercial and specially designed photoresists have been employed in *DLW* [3,4]. One such class of materials is photosensitive organic–inorganic hybrid sol–gels [5,6]. These materials can be easily prepared and, after photopolymerization, they are chemically and electrochemically inert and mechanically stable. The co-polymerization of a silicon alkoxide with another metal alkoxide has

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been shown to enhance the material mechanical stability and allow the modification of its refractive index [7,8]. The incorporation of germanium (*Ge*) alkoxides in a photosensitive sol–gel is particularly interesting, as they possess high optical transparency in the visible and near-infrared part of the spectrum [9,10]. Furthermore, *Ge* is widely used in fiber optics, making it useful in integrated microoptical circuits [11]. Recently, *DLW* fabrication of microoptical structures on the tip of the optical fiber was demonstrated [12,13]. Using a material containing *Ge*, it is possible to manufacture microoptical components of similar material contents as the core of the optical fiber itself.

In this work, we investigate the structurability by *DLW* of a Ge-containing photosensitive composite. We show that it is possible to make optically transparent and *3D* structurable material with *Ge* isopropoxide (*GIP*) content as high as 40% (w/w). The structurability properties are comparable to the ones of the best *3D DLW* structurable materials to date [14,15]. We found the optimum *GIP* content, regarding structurability and measured its refractive index and optical transparency. Though *DLW* has already been successfully employed in above mentioned fields, applications in microoptics are still limited [16,17], and not much has been done to process hybrid materials for manufacturing complex, integrated microoptical devices [18,19]. We present experimental results into structuring MicroOptical Components (*MOCs*) using this material. These are *PhC* templates, Aspheric MicroLenses (*AML*) and prisms. Lastly, some sub-100 nm features are produced. To date this is the best laser structuring resolution achieved using a hybrid material, demonstrating the potential of the composite in very high resolution structuring.

## 2. Materials and methods

### 2.1. Material preparation and characterization

The organic polymerizable monomer used in this work was methacryloxypropyl trimethoxysilane (*MAPTMS*, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, Sigma–Aldrich). The inorganic network former was based on the alkoxysilane groups of *MAPTMS* and *Ge IV* isopropoxide ($Ge[OCH(CH_3)_2]_4$, 97%, Sigma–Aldrich). The hydrolysis of *MAPTMS* was performed using *HCl* solution 0.1 M at 5% (w/w). Then *GIP* was slowly added to the mixture. The molar ratio of *MAPTMS:GIP* was varied between 4:1 and 1:1. The photoinitiator (*Irgacure 369* (*Ciba*) or *4,4′-bis*(*dimethylamino*)*benzophenone* (Sigma–Aldrich)) was added at 1% (w/w) concentration to the *MAPTMS* in order to increase material photosensitivity and achieve optimal structuring parameters [20]. After stirring for 24 h, solution was filtered using 0.22 μm syringe filters. The samples were prepared by spin-coating (1000–4000 rpm for 60 s) or drop casting on microscopic cover glass or quartz substrates, and the samples were dried in ambient conditions for 72 h prior to photopolymerization. Isopropanol was used as a solvent to reduce the viscosity of the material for the spin-coating procedure. This way thin films (500–6000 nm thickness) or droplets (∼50 μm) of gel could be prepared needed for material optical properties measurements or *DLW* fabrication experiments. The photopolymerization of thin films was performed exposing the samples to 248 nm 15 ns *KrF* excimer laser irradiation. Development was performed in pure *4-methyl-2-pentanon* for at least 1 h and rinsed in isopropanol to completely remove the residue of the non-exposed material. The prepared composite was stable and used in less than 2 weeks. The refractive index of the sol–gel films at 632.8 nm was determined from an m-line prism coupling experiment using a *HeNe* laser [21].

### 2.2. Direct laser writing method

The procedure for the fabrication of *3D* micro/nanostructures by multiphoton polymerization has been described by several groups [1,2]. In this case, the light source used was a *Ti:Sapphire* femtosecond laser operating at 800 nm wavelength. The employed fabrication setups based on solid state diode-pumped femtosecond laser oscillators are described elsewhere [8,13]. The structures were fabricated in a layer-by-layer fashion. *3DPoli* software was used for the full automation of the fabrication process.[1] The produced micro/nanostructures were investigated using scanning electron microscopy (*SEM*). 10 nm gold layer was sputtered on the samples to provide electrical conductivity. The focal distance of the microlenses was measured using an established method, and its principle is shown in Fig. 1(d) [22].

## 3. Results and discussion

### 3.1. Material transparency and refractive index

It has been shown that by changing the ratio metal alkoxide ratio, it is possible to tune the

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