



Sub-wavelength self-organization of chalcogenide glass by direct laser writing



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ABSTRACT

Chalcogenide glasses (ChGs) are quoted as a key material for the development of infrared technologies due to its unique optical properties. The right choice of processing technique is crucial to reach progress in this field, especially when achieving the nanoscale, to further comprise new functionalities to ChGs. Herein, we demonstrated the sub-wavelength self-organization of ChG with hierarchical nano/micro control by using ultrafast laser processing, representing an important step towards the fabrication of photonic devices of tailored architectures. Particularly, those findings are demonstrated through laser induced forward transfer with femtosecond pulses applied to As₂S₃ thin films, which enabled the controlled deposition of nanostructures within a micrometric region (with resolution on the order of 3 μm). The self-organized patterns exhibits periodicity with subwavelength dimensions on the order of $\lambda/4$, with $\lambda \sim 800$ nm. In the best of our knowledge, the investigation addressed herein correspond to the first demonstration of self-organization of ChG using direct laser writing, extending the applicability of the method for materials nanostructuring.

1. Introduction

Self-assembly provides a pathway for material nanostructuring, extending its applicability to a wide range of technological interests, encompassing life sciences, physical science and engineering [1]. Considerable advances have been achieved regarding the self-assembly of metals and polymers, which were demonstrated to be valuable for magnetic recording, electrochemical sensing, drug delivery and several electronic components [1–4]. Nonetheless, the class of glassy materials has been overlooked despite its relevance for optics and photonics areas. Particularly, chalcogenide glasses (ChG) are important materials for mid-infrared technologies, including the development of optical fibers, photonic crystals and integrated optical circuits [5–8]. Therefore, due to the need of optical elements for the infrared region, the search for techniques capable of processing chalcogenide glasses (ChGs) has increased significantly [9,10].

Among the available techniques to produce optical devices in ChGs, direct laser writing with femtosecond pulses has excelled on account of its ability to achieve the material processing at micrometer scale, without requiring the use of masks and clean rooms, as opposed to lithographic approaches [11]. Because nonlinear optical phenomena dominates the laser-matter interaction when ultra-short laser pulses are employed, the material modifications are confined to the focal volume,

enabling, for instance, the fabrication of micrometric waveguides into the bulk of ChGs [12,13], as well as nanowires [14] and optical gratings [15].

Despite the progress on the laser processing of chalcogenide glass, the obtainment of sub-micrometric or nanostructures suitable for practical applications is still challenging because high intense laser pulses usually causes material ablation and degradation of its properties, mainly when interacting with thin film specimens. Thus, little attention has been given to thin films, which are interesting not only because of the demand for smaller and smaller sizes, but also due to their ease of synthesis, as in solution-processing methods [16–19]. Above all, laser nanostructuring of ChG thin films have not been achieved, which has an important role for the advance of infrared technologies. In this sense, this paper brings out the self-organization of chalcogenide sub-micrometric structures by using ultra-fast laser processing. Self-organized sub-wavelength structures are deposited in micropatterns predetermined by the laser scanning, allowing the design of complex geometries with the hierarchical micro/nano control.

Specifically, such achievement was accomplished by means of laser induced forward transfer (LIFT) with femtosecond pulses (called fs-LIFT), which is a method mainly used to transfer metallic pastes, polymers or biomaterials [20,21]. Therefore, the investigation addressed herein corresponds to one of the first results on appropriate

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LIFT of glasses along with refs. [22,23]. Moreover, it is the first one to our knowledge to report the controlled deposition of glasses within the micrometer scale (with resolution close to $3\ \mu\text{m}$) with an additional assembly, whose periodicity achieve sub-wavelength dimensions, being on the other of $\lambda/4$, where $\lambda \sim 800\ \text{nm}$ from a Ti:Al₂O₃ fs-laser. Those results extend the applicability of direct laser writing methods beyond current limitations, representing a top-down approach for materials self-organization in nanoscale.

2. Materials and methods

Laser induced forward transfer (LIFT) with femtosecond pulses was used to perform the processing of ChG thin films. The method consists on the backside irradiation of a donor substrate containing the target material to be transferred to a second substrate, called receptor, located in close proximity or in contact with the first one. Our experimental setup consists in a femtosecond Ti:Sapphire laser oscillator (50-fs pulses), centered at around $800\ \text{nm}$, with a repetition rate of $5\ \text{MHz}$, focused at the interface of the donor and the receptor substrate, using a $40\times$ (0.65 NA) microscope objective. Both donor and receptor substrates were maintained in contact and placed on an x - y - z translation stage, moving with constant speed of $50\ \mu\text{m/s}$. Such speed provides 3×10^5 pulses-per-spot (considering the spot size $\sim 3\ \mu\text{m}$) and was chosen based on preliminary results providing better material confinement in a central line. A CCD camera aligned to the microscope objective allows monitoring the entire process. The pulse energy was varied between 10 and $44\ \text{nJ}$, by using a combination of a half-wave plate and a linear polarizer, to determine the best conditions for the material transfer. For those experimental conditions, the peak intensity is estimated in the range of 5.7 – $25\ \text{TW/cm}^2$, depending on the applied pulse energy. Fs-LIFT was carried out using a Gaussian beam with linearly polarized light at three conditions: parallel, orthogonal and 45° to sample scanning direction.

The donor thin film, with a thickness of approximately $500\ \text{nm}$, was prepared by spin-coating the solution of arsenic trisulfide (As₂S₃ alfa aesar 99.999%) in n -propylamine (C₃H₇N Sigma-Aldric > 99%) with a concentration of $133\ \text{g L}^{-1}$ on glass slides, followed by its annealing at $60\ ^\circ\text{C}/1\ \text{h}$ and $110\ ^\circ\text{C}/7\ \text{h}$ for solvent removal and glass densification, respectively. The complete synthesis of the As₂S₃ solution and thin films were carried under vacuum, as detailed in Ref. [19]. The transferred material over the receptor substrate (glass slide) was characterized by atomic force microscopy (AFM, nanosurf - easyScan2) to assess the surface morphology, UV-VIS spectroscopy (Shimadzu-1800) to check the optical constants, energy-dispersive X-ray spectroscopy (EDS, Apollo X Silicon Drift Detector in a SEM) and micro-Raman spectroscopy (Witec, Alpha 300, $\lambda_{\text{exc}} = 632.8\ \text{nm}$) to determine its composition and structure, respectively.

3. Results and discussion

In order to obtain ideal fs-LIFT conditions, the pulse energy (E_p) was varied in the range of 10 – $44\ \text{nJ}$, while scan speed was kept at $50\ \mu\text{m/s}$. The transfer of ChG (As₂S₃) occurs in the form of distinct particles, whose size and distribution are affected by E_p , as demonstrated in Fig. 1. The profilometry data shown in Fig. 1a reveals that the thickness of the transferred material can be changed from approximately 100 to $340\ \text{nm}$, by increasing the pulse energy from 20 to $44\ \text{nJ}$. The material transfer can be classified in two regimes, one for low pulse energy, $10 \leq E_p \leq 20\ \text{nJ}$, corresponding to a homogeneous particle distribution about a central line; and one for higher pulse energy ($24 \leq E_p \leq 44\ \text{nJ}$), which causes a non-uniform distribution, represented by a central depressed region surrounded by bigger particles. Both regimes are better visualized through the SEM images displayed in Fig. 1b for $E_p = 20\ \text{nJ}$ and Fig. 1c for $E_p = 44\ \text{nJ}$, featuring the material deposition with low and high pulse energy, respectively. For $E_p < 10\ \text{nJ}$, no significant transfer of the As₂S₃ was detected. We found the optimal energy for the

spatial control of ChG transfer to be $20\ \text{nJ}$, which enables a uniform deposition of spherical particles with diameters of about $200\ \text{nm}$, distributed in a $2.8\ \mu\text{m}$ -wide central line, whose length is defined by the laser scanning. This pattern is also illustrated by the AFM image in the inset of Fig. 1a, which clearly shows the transfer of ChG particles on the receptor substrate and confirms its controlled deposition in nano and micro-scale.

To investigate the chemical nature of the transferred material, EDS – energy dispersive x-ray spectroscopy were carried out, indicating the presence of $38.8\ \text{at\%}$ of Arsenic and $61.2\ \text{at\%}$ of Sulfur, with uncertainty below 5% , revealing that the stoichiometry of the donor (As₂S₃) is kept after the fs-LIFT. The structure of the transferred As₂S₃ and the donor As₂S₃ films were evaluated by Raman spectroscopy, as displayed in Fig. 2. The spectra present the typical broad band centered at $350\ \text{cm}^{-1}$, assigned to the vibrational modes of AsS_{2/3} pyramids along with smaller bands/shoulders at $\sim 198\ \text{cm}^{-1}$ and $240\ \text{cm}^{-1}$ indicating the presence of As₄S₄ units. The vibrational band at $495\ \text{cm}^{-1}$ is due to S₈ rings [19,24,25]. Moreover, the overall feature indicates the preservation of the dominant basic structural units in the network of the ChG deposited through fs-LIFT and the absence of long-range order, as seen in the donor film.

No significant alteration on the optical properties were observed when analyzing the absorbance spectra of the donor and transferred material; the determined optical band gap are $2.34\ \text{eV}$ ($530\ \text{nm}$) and $2.32\ \text{eV}$ ($533\ \text{nm}$) for donor and transferred As₂S₃, respectively. Although oxidation of ChG when irradiated in air with photons with energy above the optical band gap have been observed, the As₂S₃ particles deposited herein are free of oxidation, confirmed mainly by EDS and Raman measurements. Thus, the application of fs-LIFT for processing ChG not only enables micro/nano transfer in pre-determined regions, but also avoid oxidation and changes in its structure and properties.

Besides preserving the properties of the original material, the deposited ChG also displayed a periodic sub-micrometric assembly, as demonstrated in the AFM images of Fig. 3. We found that the organization of the As₂S₃ droplets depends on the laser polarization, which was performed with linearly polarized light parallel (a), orthogonal (b) and at 45° (c) to the sample scanning direction, according to the indication arrows in Fig. 3. As one can note, the organization always occurs perpendicular to the linear polarization direction. No periodicity was observed when applying circular polarization. Two-dimensional Fourier transformation applied in the AFM images of Fig. 3 showed that the spatial period is within 180 – $190\ \text{nm}$, being on the order of $\lambda/4$, demonstrating that the fs-LIFT process of ChG thin films results in the deposition of periodic pattern with subwavelength dimensions.

The periodicity seen in the material deposited herein can arise from instabilities induced by the transfer process, such as Rayleigh and/or Marangoni instabilities, which are known to govern the self-assembly in polymer films, resulting in highly ordered droplets/structures spaced at regular distances [26–28]. Additionally, as we have demonstrated the nanodroplets orientation perpendicular to the polarization, it is also possible that the periodic surface pattern is caused by inhomogeneous energy absorption in the donor substrate due to its roughness, similar to the phenomenon called of LIPSS - laser induced periodic surface structures [29,30].

Despite the similarities of the subwavelength structures shown in Fig. 3 with high spatial frequency LIPSS (HSFL), represented by periodicity smaller than $\lambda/2$ and oriented perpendicularly to the beam polarization upon the irradiation with ultrashort-laser pulses [31], it is important to mention the occurrence of nanoscale pattern in bulk ChG [32,33] and photoelectron-deposited chalcogenide films [34–36]. However, in the latter case, the authors reported a photo-tropical growth parallel to the polarization of a low-intensity light. The proper determination of the phenomena behind the subwavelength surface pattern seen herein is out of the scope of this paper, whose purpose is to show a top-down approach for material nanostructuring, represented

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