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

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ABSTRACT

Chalcogenide glasses (GhGs) 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 As_2S_3 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 applicably to a wide range of technological interests, encompassing live 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 μm) with an additional assembly, whose periodicity achieve sub-wavelength dimensions, being on the other of λ/4, where λ ~ 800 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 nm, with a repetition rate of 5 MHz, focused at the interface of the donor and the receptor substrate, using a 40× (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 μm/s. Such speed provides 3×10^5 pulses-per-spot (considering the sport size ~ 3 μm) and was chosen based on prelaminar 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 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 TW/cm², 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 nm, was prepared by spin-coating the solution of arsenic trisulfide (As_2S_3 alfa aesar 99.999%) in n-propylamine (C_3H_9N Sigma-Aldric > 99%) with a concentration of 133 g L⁻¹ on glass slides, followed by its annealing at 60 °C/1 h and 110 °C/7 h for solvent removal and glass densification, respectively. The complete synthesis of the As_2S_3 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, $\lambda_{exc} = 632.8$ 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 nJ, while scan speed was kept at 50 μm/s. The transfer of ChG (As_2S_3) 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 nm, by increasing the pulse energy from 20 to 44 nJ. The material transfer can be classified in two regimes, one for low pulse energy, 10 ≤ E_p ≤ 20 nJ, corresponding to a homogeneous particle distribution about a central line; and one for higher pulse energy (24 ≤ E_p ≤ 44 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 nJ and Fig. 1c for E_p = 44 nJ, featuring the material deposition with low and high pulse energy, respectively. For E_p < 10 nJ, no significant transfer of the As_2S_3 was detected. We found the optimal energy for the

spatial control of ChG transfer to be 20 nJ, which enables a uniform deposition of spherical particles with diameters of about 200 nm, distributed in a 2.8 μm-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 at% of Arsenic and 61,2 at% of Sulfur, with uncertainty below 5%, revealing that the stoichiometry of the donor (As_2S_3) is kept after the fs-LIFT. The structure of the transferred As_2S_3 and the donor As_2S_3 films were evaluated by Raman spectroscopy, as displayed in Fig. 2. The spectra present the typical broad band centered at 350 cm⁻¹, assigned to the vibrational modes of $AsS_{2/3}$ pyramids along with smaller bands/shoulders at ~ 198 cm⁻¹ and 240 cm⁻¹ indicating the presence of As_4S_4 units. The vibrational band at 495 cm⁻¹ is due to S_8 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 eV (530 nm) and 2.32 eV (533 nm) for donor and transferred As_2S_3, respectively. Although oxidation of ChG when irradiated in air with photons with energy above the optical band gap have been observed, the As_2S_3 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 As_2S_3 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 nm, being on the order of λ/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 λ/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
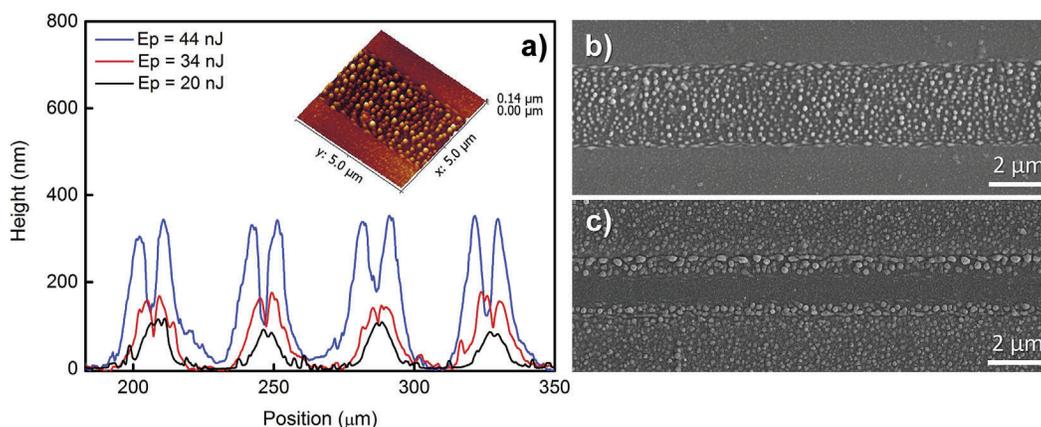
Fig. 1. Influence of the pulse energy (Ep) on the transfer of As_2S_3 using fs-LIFT. Perfilometric measurements is shown in (a) for Ep = 20, 34 and 44 nJ along with the AFM image of the deposition with the ideal condition (Ep = 20 nJ). SEM images in (b) Ep = 20 nJ and (c) Ep = 44 nJ correspond to the features obtained for low and high pulse energy deposition regime, respectively.
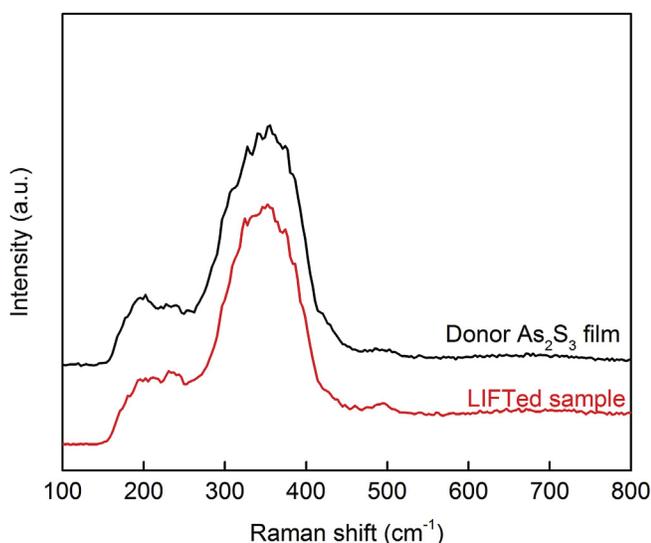

Fig. 2. Raman spectra of the donor film (black curve) and of the material transferred on the receiver substrate by fs-LIFT (red curve), showing that the laser processing does not change the structure of the As_2S_3 glass. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

by the hierarchical control of glass deposition within nano/microscale using ultrafast laser processing. It is worth to point out that subwavelength patterned structures have not been described for materials deposited via LIFT. Moreover, we have demonstrated the controlled

deposition of chalcogenide nanodroplets (< 200 nm) in the microscale, down to $3\,\mu m$ line width, confirming the potential of fs-LIFT for the design of photonic crystals for the mid-infrared region. Such application is likely to be implemented, since direct laser writing methods are experiencing lab-to-fab transfer with impact in several areas, from medicine to micromechanics and photonics [37,38]. In order to achieve this step, open questions concerning the influence of the wavelength, film thickness, focusing lens, distance between donor and receiver substrate over the resolution, particle size and periodicity of the deposited ChGs need to be solved, and are currently under investigation.

4. Conclusion

We have shown the self-organization of subwavelength glassy structures using ultrafast laser processing. Laser induced forward transfer with femtosecond pulses (fs-LIFT) revels to be a relevant top-down approach for materials nanopatterning, extending the applicability of direct laser writing methods. The methodology employed herein enabled the controlled deposition of As_2S_3 sub-micrometric structures in regions as small as $3\,\mu m$, configuring a hierarchical nano/micro deposition. Furthermore, the use of fs-LIFT shown advantages in respect to other direct laser writing methods, such as avoiding material ablation and oxidation. Spectroscopy analyses of x-ray energy dispersive spectroscopy, Raman and UV-VIS absorption confirmed that the composition, structure and optical properties of the target (donor film) are kept on the micro/nano pattern deposited by fs-LIFT. Moreover, we have demonstrated that the self-organized sub-micrometric structures, which display a periodicity of $\lambda/4$, are aligned perpendicularly to the light polarization. Therefore, besides the hierarchical control of nanostructures deposition within microscale, one are also capable to
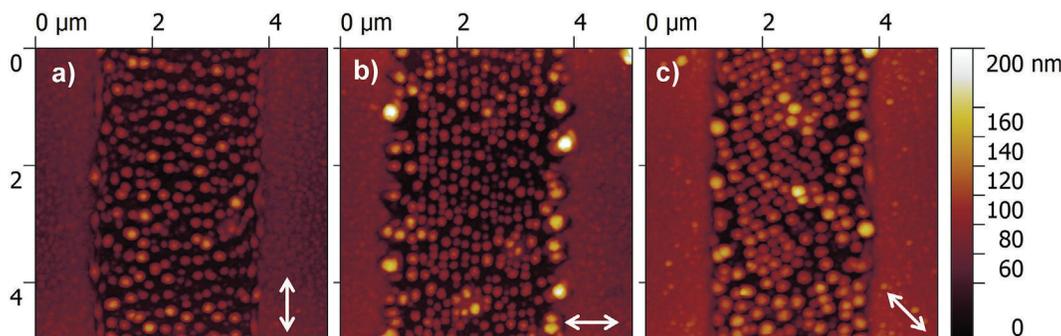

Fig. 3. AFM images of ChG deposited by fs-LIFT (Ep = 20 nJ) with linearly polarized light parallel (a), orthogonal (b) and at 45° (c) to the sample scanning direction, as indicated by the arrows.

manipulate their orientation, corresponding to an important step to-wards the development of photonic devices for the mid-infrared of tailored architectures.

Acknowledgment

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