Formation of nano-fibers and micro-spheres by femtosecond laser ablation of chalcogenide glass

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ABSTRACT

Formation of nano-fibers ranging from 30 to 300 nm in diameter and exceeding the length of one millimeter was observed during explosive ablation of As₂S₃ glass by femtosecond pulses at high fluence (> 5 J/cm²) irradiation of the 800 nm wavelength, 160 fs duration pulses in air. However, the spheres of up to several microns in diameter are found to form competing with nano-fiber formation and significantly deteriorating their morphology. The formation of these spheres is explained by the free energy minimization of explosively ablating liquid jets combined with the onset and evolution of the thermo-capillary forces at the local perturbations of the geometry and temperature. Performed thermal analysis suggests that the good nano-fiber morphology can be preserved by increasing the air pressure or ablation in water which shortens the characteristic cooling and solidification time of the liquid jets, and inhibits the development of the small geometrical perturbations into the large spheres.

Keywords: femtosecond laser ablation, nanofibers, microspheres, chalcogenide glass

1. INTRODUCTION

Fibers of sub-wavelength diameter have a great potential as effective waveguides for emerging optics and micro-photronics applications. Fibers of sub-micron diameter (Si) were also found to have significantly larger tensile strength enabling development of new micro- and nano- mechanical applications (as springs and levers). Laser ablation is one of the effective and well established methods to form different types of nano-structures, thin film structures and patterns with new functional properties. In this communication we report on formation of nano-fiber from As₂S₃ glass by ablation in air using femto-second (fs) - pulsed irradiation. Fibers of a very high aspect ratio (the length to diameter ratio) over 10⁴ were found to form. However, after laser ablation process the spheres having diameters up to several microns are also shown to form competing with the formation of nano-fibers and seriously deteriorating their morphology. Here we present the main experimental results and discuss a possible mechanism underlying the formation of the combined nano-fiber - spherical structures. The suggested mechanism and estimates reveal an experimentally feasible possibility of inhibition of the sphere formation and preserving good nano-fiber morphology in the final deposits.
Fig. 1 SEM images of the ablation path recorded at 5 J/cm² (a) and the close-up views of molten-solidified nano-structures (b, c).
In our experiments we used fs-pulses obtained from a Ti: Sapphire laser \(\text{(Hurricane, Spectra Physics)}\) operating at the 800 nm wavelength with pulse duration of \(\tau=130 \pm 10\) fs at FWHM at the repetition rate of 1 kHz. Laser radiation was focused onto the sample of \(\text{As}_2\text{S}_3\) using an objective lens of numerical aperture \(NA = 0.55\). Pulse duration at the focus was measured by GRENOUILLE technique \(\text{(Swamp Optics)}\).\(^7\) It allows to record time \(\times\) spectrum image of the pulse, and then, pulse duration (FWHM) can be retrieved by the frequency-resolved optical gating (FROG) algorithm \(\text{(Femtosecond technologies)}\). For the all retrieved pulse durations a FROG error was lower than 2 \%; pulse duration on the sample was \$160\pm15\) fs. In experiments we used a commercial \(\text{As}_2\text{S}_3\) glass. Morphology of ablated surface was observed by scanning electron microscopy (SEM). Chemical elemental analysis was carried out on a field emission SEM \(\text{(JEOL, JSM-6700FT)}\) by an energy dispersion spectrometry (EDS). Intensity of characteristic spectral regions of K-lines for S (2.18-
2.43–keV) and As (10.31-10.75–keV) were measured at 20 kV electron irradiation. Chemical analysis of fibers and microspheres revealed that their composition was identical to the initial stoichiometry of As$_2$S$_3$ glass within uncertainty of 5%.

The formation of fibers, rods, and microsphere-type structures was observed as a typical result of As$_2$S$_3$ ablation by 160–fs pulses of 800–nm wavelength at fluences larger than 5 J/cm$^2$ (see Fig. 1). Fibers from 20 to 300–nm in diameter and their bundles up to several millimeters long were routinely obtained when focal spot was placed approximately 6-8 µm beneath the surface. Fibers from 30 to 300 nm in diameter and their bundles up to several millimeters long were routinely obtained when focal spot was placed approximately 6 – 8 µm beneath the surface. This particular geometry of focusing allowed to reach high irradiance at the focus of well defined spatial cross-sections (a spherical aberration due to high refractive indices mismatch was minimized by controlling a divergence of the laser beam). Also, this geometry reduced possibility of an unwanted pre-surface air breakdown at high intensity. When the laser pulses were translated below the surface, the molten glass formed jets by ablation resulting in the fibre structures discussed here. The ablation occurred with strong crack formation (Fig. 2). When laser pulses of the same energy were focused directly onto the surface, the morphology of molten-and-quenched material had different morphology without nanofibers. It appeared from SEM observations of ablated surfaces, that such fibers were pulled from the melt bath by the droplets and liquid jets which resulted from phase explosion of super-heated melt (Fig. 1(a, b)). The fiber formation had not been observed during the ablation, but by an ex situ inspection of surface using SEM. Some of fibers had the spherical beads of 1 – 3 µm in diameter formed on them (Fig.1). Also, spheroidal droplets of different sizes having larger cross-section along the fiber were observed (Fig. 2 b).

3. DISCUSSION

Let us discuss a possible mechanism underlying the formation of the diversity of observed structures. Firstly, Figs. 1a and b suggest that initially liquid jets are formed by (i) superheated high- pressurized melt produced within fs-laser irradiated spot under the surface, (ii) cracks formation around the high pressure molten zone followed (iii) by high-pressure melt extrusion through the cracks coming to the surface. Secondly, Fig. 1 c suggests that the dynamics of their formation is also defined by interacting capillary forces strongly coupled with thermal processes involved into the cooling and solidification of a liquid jet-particle network. The involvement of the surface thermo-capillary (Marangoni) force into fs-laser materials micro-processing and formation of surface structures has been already suggested by several studies. The laser induced temperature non-uniformity is also known to destabilize the jet surface and lead to the drop formation in ink-jet printing technology. In general, the tendency for the formation of spherical particles (Fig. 2) from the liquid jets corresponds to the free energy minimization. Along with this physical principle, an important role in the dynamics of observed structure formation can be obviously attributed to the effects played by the small initial perturbations in the temperature and liquid jet geometry. In particular, let us consider a simplistic small perturbation model for surface tension forces acting on the initially cylindrical liquid element subject to the small radius and temperature perturbation between $x$ and $x + dx$:

$$dF = 2\pi \dfrac{d(r\sigma)}{dx} dx = 2\pi \left( \sigma(T) \dfrac{d(r)}{dx} + r \dfrac{d\sigma}{dT} \dfrac{dT}{dx} \right) dx , \quad (1)$$

where $r(x)$ is the fiber radius and $\sigma(T)$ is the dependence of surface tension on temperature $T$. Integration of $dF$ over the area of perturbation, $l$ (where $d\sigma/dx\neq0$ and $dT/dx\neq0$) gives the following expression for the induced capillary force:

$$F = 2\pi \left[ r(x) \dfrac{d\sigma}{dT} \dfrac{dT}{dx} + \sigma(x) \dfrac{dr}{dx} \right] dx . \quad (2)$$

This expression shows that this capillary force initiated, for instance, by a small geometrical perturbation, has a positive increment tending to drag the liquid material into a larger sphere. Such geometrical perturbation can be obviously due to the collision with a small particle enlarging instantly local jet diameter. For instance, let us consider the increment of capillary force Eq. (2) regarding a small spherical perturbation defined by $r(x) = \sqrt{(R_0 + \delta R_0)^2 - x^2}$ for $0 < x \leq x' = \sqrt{(R_0 + \delta R_0)^2 - R_0^2}$, where $\delta R_0$ is the perturbation and $R_0$ is the initial jet radius remaining unperturbed for
Performing the integration of Eq. (2) and assuming that initially \( \frac{dT}{dx}=0 \) one finds that the resulting capillary force, \( F = -2\pi\sigma R_0 \), directed towards the center of the perturbation has a positive increment of the absolute value \( \partial F / \partial R_0 = 2\pi\sigma \), meaning that the larger the perturbation the larger the capillary force developed by this perturbation.

If in making local perturbation the colliding particle has a different temperature causing a local temperature perturbation as well. However, in the considered case of explosively formed high temperature jets cooled by the air even the formation of the geometrical (\( T \)-uniform) perturbation leads with time to the development of temperature non-uniformity which able to interfere with initial capillary force and to make the structure evolution more complex. In particular, the possibility of the onset of the significant temperature non-uniformity follows from a one-dimensional heat conduction equation for thin bodies with the changing radius. Taking into account the heat conductance along the jet and heat dissipation towards the gas by heat conductance and radiation this equation writes as:

\[
\rho_f c_f \frac{\partial T_f}{\partial t} = -\frac{1}{\pi R(x)^2} \frac{dJ}{dx} \xi \frac{2}{R(x)} [g_g + \varepsilon \sigma_g (T_f^4 - T_g^4)] , \quad (3)
\]

where \( J = -\pi R(x)^2 k_f dT_f / dx \) is the heat flux through the cross-section at \( x \), \( k_f \) is the heat conductance (0.2 W/m), \( \rho_f \) is the density, \( c_f \) is the specific heat, \( \varepsilon = 0.5 - 0.9 \) is the emissivity, \( \sigma_g \) is the Boltzman constant and \( g_g = -k_g \partial T_g / \partial r \) is the heat flux density to the air (formally this value is defined by the equation \( \rho_g c_g \partial T_g / \partial t = \nabla (k_g \nabla T_g) \) coupled at \( r=R(x) \) with the temperature of the jet by \( T_g = T_f \).

We have carried out the calculations of the temperature distributions along the cooling jet having the spherical perturbation. For \( g_g \) we use an order of magnitude estimate based on the length of the thermal wave penetration from the hot filament into the air, \( \lambda_f \approx \sqrt{\alpha_g / \rho_g c_g} \) as:

\[
q_g = -k_g \partial T_g / \partial r \approx \frac{k_g}{\lambda_f} (T_f - T_g) = \frac{\frac{k_g}{\lambda_f}}{T_f - T_g} . \quad (4)
\]

Eqs. (3) and (4) shows that the temperature non-uniformity develops because the perturbed part has a lower cooling rate, \( \partial T / \partial t \) as compared with the unperturbed jet. The heat conductance acting along the jet tends to smooth out this effect. However, the low heat conductance of this material \( =0.2 \text{ W/m K} \) (known, in fact, only for solid and accepted in our calculations for liquid state) can lead to the significant temperature non-uniformity developing with time at the geometrical perturbation.

To illustrate this effect we show in Fig. 3 the temperature distributions along the jet of radius \( R_0=200 \) nm and having initial spherical perturbation with radius \( R=2R_0=400 \) nm at the near sublimation temperature \( T_{\text{in}}=900 \) K and cooling down by the air at \( T_g=300 \) K and atmospheric pressure. The temperature distributions are given along the jet at different moments. These distributions show that a very significant temperature non-uniformity develops at the perturbation resulting from the different cooling rates of (i) the perturbed \( (x < 0.3 \mu m) \) and (ii) unperturbed parts of the fiber. However, with time when the temperature tends closer to \( T_g \) this non-uniformity decays.

The behavior of the jet (fiber) temperature is given in Fig. 4 showing maximal and minimal temperature and the temperature difference. The above figures suggest that during the formation of structures observed in our experiments different effects can interfere. Let us discuss main features provided by the above estimates. The surface tension of As\(_2\)S\(_3\) is not known. However, the typical ranges for surface tension values for melts are held within the ranges of \( \sigma = 0.1-1 \) N/m and \( d\sigma/dT = -0.1-1 \) mN/m K. Thus, the initial perturbation of \( \Delta R_0=200 \) nm is able to develop a capillary force of \( \approx 2\pi\sigma R_0 \) dragging the liquid jet into spherical particle. In contrast, the developed temperature non-uniformity outside of this spherical perturbation, \( \Delta T \approx 20 \) K, can develop the force along the unperturbed fiber of \( \approx 2\pi\sigma \Delta T d\sigma / dT \). However, the characteristic time of the development of this force corresponds to the time of the development of the temperature non-uniformity at the initial perturbation. Thus, the perturbed and unperturbed parts of the cooling jets experience forces acting.
in different directions and moments, tending to break the jet into the drops, and providing observed complex nano-fiber-sphere structures. That is, during cooling the jet-particle system changes dynamically through all the process. In particular, the force associated with temperature gradient along the jet, can start formation of a new geometrical perturbation within several microns from the initial perturbation, defined by the temperature non-uniformity. By initiating a new geometrical perturbation, this thermally-induced force should also be initially enhanced by the arising stronger geometrical component \( (\sigma(x)dr/dx) \). However, the development of this radial perturbation should decelerate with time as the temperature fall in the perturbed area changing the direction of \( dT/dx \) (as well as the associated capillary force). These initial non-uniformities evolve in time and space until the moment when the structure elements achieve the temperature of solidification. The simulation of this free boundary problem to follow possible geometrical evolution of the liquid jet-particle network into the final solid structure would require a very significant computational effort including the simulation of non-isothermal viscous flows. However, we should stress here that the characteristic time of formation of the liquid spheres corresponds to the development of capillary driven viscous flows to
an order of magnitude defined by \( \tau \approx l^2/\nu \) (where \( l \) is the characteristic size of the perturbation and \( \nu \) is the kinematic viscosity. For high temperature melts \( \nu \approx 10^{-7}-10^{-6} \text{ m}^2/\text{s} \) which together with the characteristic size of the observed perturbations, \( l \approx 1-3 \mu \text{m} \), gives the typical value of \( \tau \approx l^2/\nu \approx 10 \mu \text{s} \). This value being much smaller than the characteristic cooling time of the liquid jet \( (\approx 100 \mu \text{s}, \text{Fig. 4}) \) shows that for the given experimental conditions the local perturbations have enough time to develop into large spheres prior to the temperature loss and solidification.

The considered perturbation and thermal model suggests an experimentally feasible way of inhibition of spherical particles formation (and resulting nano-fiber morphology deterioration) by shortening the cooling time and making the liquid jet to solidify before the occurring perturbations develop into the large spheres. In particular, Eqs. (3) and (4) suggest that the cooling time of the liquid jet towards the temperature of solidification, \( T_{sol} \), depends strongly on the air pressure. In effect, neglecting in Eq. (3) the radiative component one can get an estimate of the solidification time as:

\[
\tau_{sol} = \frac{1}{16} \frac{(R_s g_s \rho_g)}{\rho_s c_s k_g} \left[ \ln \frac{T_g - T_s}{T_{sol} - T_g} \right]^2, \tag{5}
\]

which gives the value of \( \tau_{sol} \approx 100 \mu \text{s} \) agreeing with the simulation.

This estimate explicitly shows that \( \tau_{sol} \propto 1/P_g (\rho_g \propto P_g) \) and the lower the air pressure the lower the cooling rate and the larger the time provided for the formation of spherical particles. In contrast, the high air pressures (>10 at.) can shorten the solidification time \( (\tau_{sol} \approx \approx 10 \mu \text{s}) \) enabling the fiber solidification prior the large spheres can form. The fast cooling and decay of the temperature non-uniformity at the final stage (shown in Fig 4) makes negligibly small the effect of surface tension associated with \( dT/dx \).

Eq. 5 shows that in contrast with 200 nm radius jet requiring about 100 \( \mu \text{s} \) for solidification, a 20 nm radius jet would solidify within only 1 \( \mu \text{s} \). This explains why the small diameter fibers were found of more uniform diameter over extended length without spherical structures on them. Finally, Eq. (5) suggests that the explosive ablation in water would allow one to decrease the solidification time of 200 nm fibers to \( \tau_{sol} \approx 1 \text{ ns} \) taking into account significantly higher values of density, specific heat and heat conductivity of the water as compared with the air. Additionally, the rapid temperature fall increases dramatically the melt viscosity inhibiting capillary driven melt flows and the development of surface irregularities, and helping one to enhance the morphology of the nano-fibers in order to meet, for instance, rigorous requirements for using them for optical waveguide and micro-photonics applications.

### 4. SUMMARY

In conclusion, the experiments and theoretical analysis of femtosecond ablation of chalcogenide glass reveals competing mechanisms involved into the formation of complex nano-structures consisting of nano-fibers and microspheres. Given estimates suggests conditions under which the thermo-capillary formation of microspheres can be inhibited by the enhanced solidification of the liquid jets explosively formed by the laser ablation.

### REFERENCES