Electrospinning of nanofibrous layers of As-S chalcogenide glass

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ABSTRACT

We report on electrospinning of $\text{As}_3\text{S}_7$ chalcogenide glass from propylamine solution. The prepared glass layers consist of nanofibers with a typical diameter of ~100 nm. The deposited layers are highly porous from the nature of the electrospinning process. The calculated effective-refractive index value of the layers is $n \approx 1.165$, at $\lambda = 1550$ nm; assuming 87 vol.% of the air and the bulk glass index $n = 2.27$ at the same wavelength. In contrast to the continuous 2-micron thick spin-coated layer, which had the absorption edge near 420 nm, the 10-micron thick porous nanofibrous layer had no significant absorption edge at all. The relative stiffness of electrospun glass nanofibers was found to be 98% of the value measured for the bulk glass of the same composition. So far, electrospinning is the only solution-based technique, which directly deposits solvent-free chalcogenide glass layers with no need for any post-deposition annealing.

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KEYWORDS

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Introduction

In recent two decades, researchers all over the world have been relooking at a century old process \cite{1–3}, currently known as electrospinning, that is able to produce continuous fibre layers with nanometer to micrometer diameter. Nanofibers and nanowires, large surface to volume ratio, have the potential to significantly improve current technology, for example catalysis, tissue scaffolds \cite{4}, protective clothing, filtration and nano-electronics \cite{5}, etc. Electrospinning is able to fabricate various nanofiber assemblies \textit{in situ}, which allows for customization of nanofiber assemblies to meet the requirement of specific applications. Other methods of fabricating nanofibers, such as phase separation \cite{6} and template synthesis \cite{7}, cannot match electrospinning in terms of its versatility, flexibility and ease of nanofibers production. Of the major classes of materials, electrospinning is able to produce nanofibers of polymers, composites, semiconductors and ceramics \cite{8, 9}. A good summary of papers on electrospinning, and nanofibers fabrication can be found in the book by Ramakrishna et al. \cite{5} (and references therein). The fundamentals of electrospinning process, influence of spinning conditions on the resulting morphology, and characterization of nanofibers for various applications can be found in Refs. \cite{10–12}. Recent research effort in electrospun fibers has been focused on exploring new materials which can be spun, characterization of the fibers and identifying new applications of the fibrous materials. It is important to fabricate various fibrous assemblies, because the fiber arrangement has significant effect on the performance of new devices. The development of the ordered (aligned) nano-grooves and assemblies has been shown to influence cell proliferation and morphology \cite{13}, and found application in the form of aligned fibers in muscle regeneration \cite{14}.
Most produced electrospun nanofibers are based on polymers or inorganic materials such as crystalline semiconductors [8, 9]. There are a few examples of electrodeposition of glasses [15–17]. Electrospinning of silica glass nanofibers was done by using a technique resembling sol–gel process with a calcination step after the deposition [15]. Low melting point borate glasses were prepared in the form of nanofibers by melt-spinning process at temperature of 850 °C [16]; such high temperatures are necessary in order to have low viscosity melt suitable for electrospinning. Glass nanofiber materials can also be prepared by pyrolysis of polymeric nanofibers such as SU8 resist, for example as it was demonstrated by J. E. Clark for glass-carbon nanofibers [17].

Preparation of polycrystalline semiconducting chalcogenides nanofibers, among the existing chalcogenide materials, has been reported: (i) by electrospinning of a polymer followed by a galvanic displacement of Bi₂Te₃ [18] used for thermo-electric applications, (ii) by electrospinning from solution mixtures with polymers, and (iii) by electrospinning of semiconducting chalcogenides such as Bi₂S₃, ZnS [19] for applications in novel sensors, super-capacitors, or batteries.

In this paper, we describe preparation of isolated nanofibers and/or nanofibrous layers of amorphous chalcogenide [20] As₃S₇ by electrospinning from propylamine solutions of the glass. The layers were deposited directly without a need for employing other processed such as sintering or pyrolysis of precursors or galvanic displacement of polymer nanofiber templates for inorganic material as it is usual in the case of fabrication of nanofibrous layers of semiconducting chalcogenide materials [18, 19].

**Experimental**

Chalcogenide glass, mass of 1 g, of the composition As₃S₇, was spontaneously dissolved in 2 mL of propylamine at room temperature for 24 h. The formed solution has dark brown color and honey-like viscosity. Films were deposited by an electrostatic spinning apparatus 4SPIN® LAB1, Contipro a.s, Czech Republic. The formed solution was dispensed from a syringe with volume of 10 ml through the needle of 26 Gauge with a feeding rate ~5 μL min⁻¹. The needle was connected to a high-voltage source with a set voltage in the range of 25‒35 kV. Temperature and relative humidity in the deposition chamber was kept in the range of 22 ± 2 °C and 30 ± 5% RH, respectively. The chalcogenide glass nanofibrous layers were deposited onto a collector surface placed oppositely to the needle, as shown in Figure 1. The distance between the needle and the collector was 15–20 cm. A grounded metal plate 20 × 20 cm was used as the collector. A rotating collector, accelerated at speeds up to 4000 rpm, was used for the deposition of aligned nanofibers. Aluminum foils attached to the metal plate and the rotating collector were used as substrates. Microscope glass slides coated with conductive ITO/FTO films were used as substrates for deposition of samples intended for optical transmission measurements. Deposition times were 1, 2, 5, 10 and 20 min resulting in formation of either isolated nanofibers or nanofiber layers on the substrates. One half of the samples was then coated with 3 nm thick Au layer by thermal evaporation.

Scanning electron microscope (SEM) images revealing morphology of the glass nanofibers or nanofiber layers were recorded by using a low accelerating voltage of ~1 kV. Atomic-force microscope (AFM) was done on isolated glass nanofibers by employing a Solver Pro M (NT-MDT, Russia) device. The measurements of surface topography, atomic-force acoustic microscopy (AFAM) and force spectroscopy (FS) measurements were carried out using a high-resolution silicon cantilevers type CSG-10 (Au coating, a cone angle less than 22°; a typical force constant of 0·1 N m⁻¹) in the contact mode. The optical transmission spectra were recorded on a UV/Vis/NIR spectrophotometer Jasco 570 in the range of wavelengths from 200 to 1800 nm.

**Results and discussion**

Macroscopically, all prepared nanofibrous samples look as continuous yellowish layers (Figure 1). Nanofibrous morphology of the electrospun chalcogenide glass layers was confirmed by using the SEM as shown in Figure 2. Figure 2, parts (a) and (b) shows isolated nanofibers of As₃S₇ glass deposited on Al foil. The deposition time for these samples was 1 min. Figure 2, parts (c)–(f) shows unaligned nanofibers, parts (c) and (e) – the metallic plate...
collector substrate, and aligned nanofibers, parts (d) and (f) – the rotating collector substrate, orientations of the glass nanofibers in 10 μm thick layers spun for 20 min. The electrospinning process ran smoothly, resembling the deposition process of polymer nanofibrous layers from solutions. The solution of As$_2$S$_3$ glass could be spun without applying any of the supporting procedures, e.g. co-spinning with easy spinable material, air blowing, and external drying, which are used to help unspinable solutions to form nanofibers. Since the glass solution viscosity and low molecular weight of the glass structural units, the yield of the electrospinning process is rather low (at low spinning rates of ~5 μL min$^{-1}$) in comparison to the spinning efficiencies which can be achieved for well-spinable polymers such as PVA and PEO.

Figure 3(a) shows comparison of optical transmittance spectra of the chalcogenide As$_2$S$_3$ glass nanofibrous layers after 1, 2 and 10 min of deposition, a 2 μm thick spin-coated layer of As$_2$S$_3$ glass, a 100 nm thick spin-coated layer of As$_2$S$_3$ glass (both spin-coated layers were deposited onto microscope slides; annealed at 120 °C for 10 h; details of the spin-coating deposition and the densification process of the layers can be found in Ref. [21]) and the As$_2$S$_3$ bulk glass. In the high absorbing region of the glass, i.e. 400–470 nm, the continuous spin-coated layer has the absorption edge near 420 nm, while the porous nanofibrous layer has no significant absorption edge at all. This is because the nanofibrous layer is highly porous and its effective-refractive index is the combination of the indices of the air and the glass. The
T. KOHOUTEK ET AL.

~4 nm; the layer deposited for 10 min shows the blue shift of $\Delta \lambda_{\text{SPR}} \approx 37$ nm. The SPR band intensity decreases with increasing thickness of the deposited As$_3$S$_7$ glass nanofibrous layers.

The atomic-force microscopy measurements performed on the isolated As$_3$S$_7$ nanofibers reveal the typical diameter of the nanofibers to be in the range of 100–130 nm; the length was estimated in the range of 1–15 μm (Figure 4). Figure 4(a) and (b) show topography of the isolated As$_3$S$_7$ nanofibers, i.e. for 1 min deposition, scans taken from 7.5 × 7.5 μm$^2$ and 2.5 × 2.5 μm$^2$ areas, respectively. Figure 4(c) shows a profile, extracted from Figure 4(a), of a representative nanofiber with the height of the probed nanofiber to be ~115 nm and its width ~110 nm. AFM technique is capable of recording information from the sample surfaces in various modes including the acoustic-AFM (AFAM) AFAM signal corresponds to the shift of the flexural resonance of the tip-sample system due to the changes of the surface and near sub-surface local elastic moduli of the material responding to the forced out-of-plane vibration emitted by an external ultrasound transducer [22]. The tip is repulsed in the linear part of the force-distance curve, which is related to the Hooke’s law ($F = -k \times \Delta$), and the slope corresponds to the stiffness of the material. The relative stiffness of the As$_3$S$_7$ bulk glass, a spin-coated As$_3$S$_7$ thin film annealed at 120 °C for 10 h and the electrospun As$_3$S$_7$ nanofiber (time?) was estimated from the slope of the lines in the plot of the deflection of the tip versus the measured piezo-crystal displacement. The curves, plotted in Figure 4(d), represent the averaged values recorded from five consecutive measurements on five different places of the samples; parts of the nanofibers firmly attached to the substrate were measured.

The stiffness of the As$_3$S$_7$ nanofibers is ~98% of the stiffness values obtained for the bulk glass. The relative stiffness of the well-annealed spin-coated film, still containing noticeable amount of the solvent, was determined to be ~89% of the value determined for the bulk glass. The glass nanofibers have stiffness of the bulk glass, despite the fact that the nanofibers did not undergo any post-deposition annealing procedure. This is the indirect evidence for obtaining the solvent-free chalcogenide glass layers by electrospinning process. So far, solvent-free layers of chalcogenide glasses have not been achieved by any of the other solution deposition techniques [23, 24].

The common limitation for the use of solution-processed chalcogenide glasses in the real applications, for example as waveguides, ring resonators and in nonlinear optical devices, stems from the inefficient release of a solvent, typically butylamine and propylamine, from the glass network even after pro-long annealing at temperatures close to the glass-transition temperature [23]. This is the issue especially for spin-coated and ink-printed thin-film chalcogenide glass optical components

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**Figure 3.** (a) Optical transmittance spectra of chalcogenide As$_3$S$_7$ glass aligned or unaligned nanofibrous layers after 1, 2 and 10-min deposition onto the silica glass slides substrates coated with ITO/FTO are shown in comparison with 100 nm and 2 μm spin-coated layer onto a microscope slide, and the bulk glass. (b) Optical transmittance spectra of the chalcogenide As$_3$S$_7$ glass nanofibrous layers after 1, 2 5 and 10 min of deposition are shown in comparison with the same layers coated with a 3 nm layer of gold and a 3 nm single-layer of gold f.

Notes: The characteristic surface plasmon resonance of Au is apparent near $\lambda = 670$ nm for all coated samples with a slight blue shift with the increasing nanofibrous As-S glass layer thickness.
advanced device materials

5

Atomic force microscopies revealed the typical diameter of the nanofibers around 100 nm and the lengths in micrometer order for the isolated nanofibers deposited for 2 min. The relative stiffness of As$_3$S$_7$ glass nanofibers was found to be ~98% of the value for the bulk glass, which promises a good material mechanical stability in potential applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 4. (a) and (b) AFM topography of chalcogenide As$_3$S$_7$ glass nanofibers deposited for 2 min. (c) The profile recorded from the nanofiber shown in part (b). (d) The dependence of the tip deflection on the piezo-displacement; the region of the repulsive interactions is used to compare the relative stiffness of the As$_3$S$_7$ bulk glass, the well-annealed spin-coated film and the electrospun chalcogenide nanofiber (Color online).

In our opinion, electrospinning may become a new route of room temperature and annealing-free solution processing of chalcogenide glass layers. Potential application of electrospun chalcogenide nanofibers can be proposed, e.g. in (i) chemical sensing – by exploiting the high porosity and high surface area of sulfur-based nanofibers (ii) batteries, where sulfur-based compounds are proposed as the promising cathode materials for high-capacitance batteries in combination with high-performance solid-state electrolytes (iii) optics by exploring the optical and optomechanical properties of chalcogenide glass nanofiber layers and aligned nanofibers.

Conclusions

We have clearly demonstrated that solvent-free nanofibrous layers of chalcogenide As$_3$S$_7$ glass can be electrospun from propylamine solutions at room-temperature, in the air atmosphere and without a need for post-deposition annealing. Electrospinning of the glass nanofibers from amine solutions is possible mainly due to the ability of As$_3$S$_7$ glass to form a viscous solution in propylamine, high volatility of the solvent, strong effect of the electro-static field on the solvent removal from the nanofibers and finally the polymer-like structure of the glass. The electron and atomic-force microscopies revealed the typical diameter of the nanofibers around 100 nm and the lengths in micrometer order for the isolated nanofibers deposited for 2 min. The relative stiffness of As$_3$S$_7$ glass nanofibers was found to be ~98% of the value for the bulk glass, which promises a good material mechanical stability in potential applications.

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