Thin Solid Films 626 (2017) 194–199

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Electrospray deposition of quantum dot-doped $Ge_{23}Sb_7S_{70}$ chalcogenide glass films

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ARTICLE INFO

Article history:
Received 23 September 2016
Received in revised form 7 February 2017
Accepted 8 February 2017
Available online 10 February 2017

Keywords:
Electrospray
Quantum dots
Chalcogenide glass
Photo luminescence
Lab-on-a-chip

ABSTRACT

The incorporation of quantum dots (QDs) into chalcogenide glass films is attractive for their luminescent properties. Such QD-doped glass structures could serve as a compact, on-chip light source for planar photonic devices. Typical processing methods such as spin coating have limitations of excessive material waste, little control on the pattern of the film and difficulty for scale-up. To overcome these limitations, this study introduces electrospray as a more versatile processing method and has deposited QD-doped chalcogenide glass thin films. The parameters of the electrospray process are prudently chosen to ensure one or none QD is enclosed per liquid droplet. The transmission electron microscopy imaging of resultant films confirm enhanced QD dispersion with reduced aggregations. Absorption and photoluminescence characterization shows the QD-doped chalcogenide glass films prepared by electrospray maintain signature spectra of QDs from the manufacturer.

1. Introduction

Chalcogenide glasses (ChG) are well-known for their potential use as components for planar chip-based photonic devices [1–6]. Several techniques of ChG film deposition exist, such as non-solution based (thermal evaporation or pulsed laser deposition of bulk glass), or via drying of wet films often based on spin-coating (SC) of amine-based glass containing solutions [7–9]. One major advantage of solution-based approaches over other techniques is that functional nanoparticles (NPs) can be incorporated into the film by simple mixing prior to deposition. One such example is quantum dots (QDs), which are semiconductor NPs with many attractive properties, such as high photostability and broad, tunable emission that can extend from the visible to the mid-IR [10–13]. QD-doped materials have promising applications in a variety of optical systems, and can be incorporated into glass by both precipitation methods in bulk and film forms of glass and the utilization of colloidal solutions in liquid-based deposition of glass films [14]. Most of the work thus far on QD-doped glasses has been in silicate-based compositions by traditional melt-quench techniques. Several studies have demonstrated QD growth in bulk silicate glasses, as well as bulk germanate glass, and characterized the luminescent properties of the QDs [15–17]. Such materials are attractive for utilization as fiber amplifiers, saturable absorbers for lasers and ultra-short pulse generation [18–21]. In film form, applications of QD-doped glasses include photovoltaics and sensing devices [22–25]. Due to quantum confinement effects, the position of the luminescence band is tunable with the adjustment of the size of QDs [26]. A key challenge in all of these approaches is the ability to spatially disperse the QDs (whether metallic or semiconductor) within the glass matrix. Clustering resulting from poor dispersion can lead to optical scattering, absorption and if the particle is optically active, concentration quenching that limits optical function [27].

Several previous studies have explored the incorporation of QDs into ChG films for their luminescent properties, which could serve as a compact, on-chip light source for a photonic device [28–30]. The typical solution-based processing method in this study was based on SC, which offers the ability to quickly deposit relatively thick films over large areas. As noted in this and our prior work [31,32], SC has several limitations: (i) significant amounts of solution are wasted by spin-off; (ii) scale-up of SC is challenging; (iii) SC is not readily applicable on curved or uneven/stepped surfaces; and (iv) SC alone does not offer the ability to spatially pattern films.

To overcome the challenge of nanoparticle dispersion in spin-coated films, this study demonstrates nanoparticle doping in electrosprayed ChG films [33]. Electrospray is a method of atomizing conductive liquids

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http://dx.doi.org/10.1016/j.tsf.2017.02.030
0040-6090/

by applying a voltage between a liquid fed through a needle and a target substrate. The electric field applies a shear stress on the liquid meniscus and causes an elongated jet to form and disintegrate into droplets, which are generally quasi-monodispersed in the micron or nanometer size range [34,35]. Electrospray has been used previously for deposition of films such as in thin radioactive sources for nuclear research, films for inorganic and organic solar cells and organic light emitting diodes. These devices fabricated by electrospray were found to be competitive with other solution-based processing methods [36–43]. Advantages of electrospray include simultaneous spray deposition of multiple liquids to fabricate hybrid or gradient films, very little waste of solution, capability of conformal deposition on curved surface, compatible to roll-to-roll manufacturing, and potential to scale up [44,45]. Most notably, the electrospray is capable of localized deposition, similar to a direct printing method, because the spray footprint is small and can be focused by external electric field [46].

Furthermore, electrospray offers the opportunity for enhanced QD dispersion in the deposited film as compared to SC, where despite efforts to tailor particle surface chemistry, QDs still exhibit aggregation [11]. The rationale of better QD dispersion employed in the present study is based on the potential physical isolation of an individual QD in one droplet, combined with the more rapid drying kinetics of a falling droplet that limits time for aggregation to occur compared to a continuous liquid phase in SC. The aim of this study is to demonstrate electrospray as a viable method of depositing solution-derived, ChG films incorporating QDs.

2. Experimental

2.1. Fabrication of bulk glass

Bulk $Ge_{23}Sb_7S_{70}$ glass was chosen for as the parent glass composition which was to form the glass solution. Bulk target material was fabricated by traditional ChG melt-quench techniques [47]. Elemental starting materials were batched into a fused silica ampoule in a nitrogen-purged glovebox, vacuum purged for 4 h at 90 °C to remove the nitrogen and residual moisture, and then sealed in the evacuated ampoule using a methane torch. The batch was melted in a rocking furnace for 16 h at 850 °C. Glasses were quenched by removing the ampoule from the furnace and holding it upright in air until the sample pulled away from the sides of the ampoule. Glasses were annealed for 16 h at 40 °C below the glass transition temperature (T_g).

2.2. QD dispersion preparation

In order to make a stable solution of ChG in which QDs can be subsequently dispersed into, bulk material is crushed into a powder with a mortar and pestle. The powder is then mixed with an amine solvent, where dissolution can be expedited with stirring and gentle heating on a hotplate with a surface temperature of 40 °C. ChG solutions were then used to fabricate films by spin-coating or electrospray, both with and without QD doping. CdSe/ZnS QDs and gold NPs were tested in this study. First, commercial CdSe/ZnS core-shell QDs capped with octadecylamine (Ocean NanoTech,San Diego, California) in powder form were used. These QDs were dispersed in ethanolamine (ETA) at a maximum concentration of 0.3 mg/mL. Second, gold NPs (nanoComposix, Laboratory in San Diego, California) of 10 nm diameter with capping agent m-polyethylene glycol (PEG) were also tested as a high contrast imaging reference to investigate the dispersion capacity of the electrospray. The gold NPs were dispersed in a 50% water: 50% ethanolamine mixture at a concentration of 1 mg/mL. The motivation for utilizing various particles were based on the refractive index contrast of the particle with the glass as well as its expected surface chemistry and interaction in the amine solution.

In order to make QD-doped films by spin-coating and electrospray suitable for comparison, QD suspensions were mixed with a 0.05 g/mL $Ge_{23}Sb_7S_{70}$/ethanolamine solution, or by dissolving the $Ge_{23}Sb_7S_{70}$ powder directly in the QD suspension. For the CdSe/ZnS core-shell QDs, $Ge_{23}Sb_7S_{70}$ was dissolved at a concentration of 0.05 g/mL in QD suspensions ranging from 0.01 to 0.3 mg/mL (maximum amount could be dissolved). The gold NPs were mixed with 0.05 g/mL $Ge_{23}Sb_7S_{70}$ in a volume ratio of 1:1, resulting in 0.5 mg/mL $Ge_{23}Sb_7S_{70}$ and 0.025 g/mL gold NPs, respectively. Table 1 summarizes the suspension formula used in this study.

2.3. Film processing

Electrosprayed films were fabricated using QD suspensions in Table 1. Details of the apparatus has been documented previously [48]. Briefly, after mixing, the solutions were sonicated for 20 min to remove microbubbles and loaded into a 0.5 mL syringe with a 30 gauge blunt needle. The electrospray deposition was set up vertically with a 10 mm working distance between the needle and a Si wafer placed on a hotplate with surface temperature of 70 °C. Typical flow rate was 10 μL/h. The films made for photo luminescence (PL) measurements were vacuum baked for 1 h each at 100, 150, and 175 °C. We found that the removal of solvent residue is more complete at higher temperature [30], therefore only results for the samples baked at 175 °C are reported here.

2.4. Film characterization

Films were characterized using several metrics to assess film quality and optical properties, both with and without dopants. Transmission electron microscopy (TEM) was carried out with a FEI Tecnai F30. Samples were prepared by electrospraying for a short period of time, nominally ~five seconds, on ultra-thin carbon TEM grids, or by using an FEI 200 focused ion beam instrument to lift-out a slice of a blanket film and attach it to the post of a half-grid for TEM analysis. The FEI 200 utilizes a 30 kV gallium ion beam to mill the sample. Photoluminescence experiments were performed to study the time-resolved luminescent behavior of QDs. The experimental setup was built as follows a frequency tripled Nd:YAG amplified laser system (30 ps, 30 mJ @1064 nm, 20 Hz, Ekspla model PL 2143) output @1064 nm doubled to obtain 532 nm excitation. Time-resolved emission signals were analysed by a spectrograph (Princeton Instruments Acton model SP2300) coupled with a high dynamic range streak camera (Hamamatsu C7700). Steady-state photoluminescence was also tested using an Ocean Optics QE Pro FL for detection, in conjunction with a 532 nm laser with power of approximately 1.5 mW as an excitation source. This system utilizes a fiber and collimating lens positioned near the sample to collect signals, with no other optics used. In addition, a 27 lm blue LED with emission centered at approximately 449 nm and having full width at half maximum of 20 nm, was also used as an excitation source for the QE Pro FL.

Table 1
QDs and glass solutions parameters.

QDs	Initial concentration	QDs solvent	Initial glass concentration	Final QDs concentration	Final glass concentration
CdSe/ZnS	powder	/	0.05 g/mL	0.01–0.3 mg/mL	0.05 g/mL
Gold NPs	1 mg/mL	50% ETA/50% deionized water	0.05 g/mL	0.5 mg/mL	0.025 g/mL
Undoped	/	ETA	0.05 g/mL	/	0.05 g/mL