Electrospray Deposition of Quantum Dot-doped $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ Chalcogenide Glass Films

Cheng Li¹, Spencer Novak^{1,2}, Sergey A. Denisov³, Nathan D. McClenaghan³, Neil Patel⁴, Anu Agarwal⁴, Kathleen Richardson^{1,2}, Weiwei Deng⁵

¹. College of Optics and Photonics, CREOL, University of Central Florida, Orlando, FL 32816, USA

². Department of Materials Science and Engineering, COMSET, Clemson University, Clemson, SC 29634, USA

³. Institut des Sciences Moléculaires/CNRS, Université de Bordeaux, Talence 33405, France

⁴. Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

⁵. Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

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 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 $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ 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 hours 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 hours 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 hours 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 1mg/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 $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ /ethanolamine solution, or by dissolving the $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ powder directly in the QD suspension. For the CdSe/ZnS core-shell QDs, $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ 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 $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ in a volume ratio of 1:1, resulting in 0.5 mg/mL $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ and 0.025 g/mL gold NPs, respectively. Table 1 summarizes the suspension formula used in this study.

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

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 μ L/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 lumen 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.

3. Results and discussion

3.1 Electrospray deposition of QD-doped films

Previous work using SC [11] shows that QDs in solution-derived ChG films indeed exhibit luminescence, but at a reduced efficiency due to aggregation of QDs. To improve the QD dispersion, this study introduced and employed the electrospray deposition method. Electrospray has been shown to produce charged droplets from the doped glass solution postulated to assist in dispersion through coulombic repulsion between droplets [34]. The QD concentration in this study has been chosen such that there is an average of less than one QD per droplet. As one droplet falls to the substrate, a portion of the droplet's solvent is believed to evaporate, enriching the ChG glass concentration and causing a rapid rise of the droplet viscosity. This higher viscosity is believed to further arrest the movement of the QD and to provide a kinetic barrier to aggregation. As the droplets are electrically charged, they should not coalesce until they reach the substrate and lose their charge.

In order to test the hypothesis of the electrospray method in this chemical system, it is first necessary to understand the initial droplet size in the undoped solutions. To this end, a scaling law was used (Equation 1) [49] to estimate the initial droplet diameter d_0 . In Equation 1, ρ is the liquid density, ϵ_0 is the vacuum permittivity, Q is the liquid flow rate, γ is the liquid-air interfacial tension, and k is the liquid electrical conductivity.

$$d_0 = \left(\frac{16\rho\epsilon_0 Q^3}{\gamma k} \right)^{\frac{1}{6}} \quad (\text{Eq. 1})$$

Based on this equation, the estimated initial droplet diameter at a flow rate of 10 $\mu\text{L/hr}$ is 260 nm, using $\gamma = 0.049 \text{ N/m}$ (value of pure ETA) and a measured conductivity of the glass solution,

$k = 2 \times 10^{-2}$ S/m. With this information, we chose the proper QD concentration (Table 1) to ensure our target of less than one QD per droplet.

3.2 Doping with commercial CdSe/ZnS core-shell QDs

To confirm that the incorporation of QDs in our glass solutions was maintained during ES, we prepared a series of TEM images of electrosprayed QDs and QD-doped ChG solutions which were deposited directly onto Cu TEM grids. First, commercial CdSe/ZnS core-shell QDs capped with octadecylamine were dispersed in ethanolamine at concentrations of 0.2 mg/mL. The QD size was investigated by spraying pure QDs/ethanolamine on a TEM grid, with sample TEM micrographs shown in Figure 1.

Fig. 1: TEM micrographs of CdSe/ZnS core-shell QDs electrosprayed on a TEM grid for ~1 s. (a) and (b) are QDs under varying magnification. The concentration of the QDs was 0.2 mg/mL, corresponding to a nominal 645 nm separation distance in the solution, assuming ideal dispersion.

In the TEM micrographs, a total of eleven QDs were identified and measured in an effort to estimate the size of the QDs and calculate their dispersion. This resulted in an average QD diameter of 5.5 nm with a standard deviation of 0.95 nm, consistent with information provided by the manufacturer.

This dispersion of QDs was blended with $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ to a concentration of 0.05 mg/mL. This solution was electrosprayed on a TEM grid by moving the spray at a velocity of 48 mm/min over the grid, with the intention of depositing a very thin film for analysis shown in Figure 2. As

shown, this resulted in droplets of solution forming in regions of the grid. This same solution was also electrosprayed on Si substrates for luminescence studies.

Fig. 2: TEM of CdSe/ZnS QD-doped $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ sprayed on TEM carbon grid with an ES pass rate of 48 mm/min

In Figure 2, the ChG residues are clearly visible as shown in medium gray, and appear as irregularly shaped due to the merging of several droplets. Figure 3 shows part of a QD-doped glass residue under higher magnification, with a QD-containing area expanded on the right.

Fig. 3: CdSe/ZnS core-shell QDs in electrosprayed droplets of $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$, concentration of 0.2 mg/mL; this concentration predicts a 70 nm expected separation distance in the cured material

The appearance of well dispersed QDs supports our premise that electrospray has potential as a method of enabling better dispersion of NPs, especially given that these QDs are separated by as little as ~15 nm in this specific region within the film. However, despite our best effort in estimating of QD concentration, the QDs in this sample do not appear as frequently as expected,

based on cured-film separation distance of 70 nm. One possibility is that the QDs are present, but not quite visible due to low image contrast between the particles and glass matrix, as discussed previously. To realize higher contrast with similar sized particles, we changed the nature of the particles, using gold NPs.

3.3 Doping with gold NPs

Due to the limited image contrast between the QDs and the glass matrix in both of the semiconductor material studies discussed above, we chose to explore a parallel set of studies using gold NPs to confirm the dispersion capability of the electrospray. The 10-nm gold NPs decorated with m-PEG were purchased from nanoComposix, and the suspension formula is listed in Table 1. Electrosprayed films were prepared using a flow rate of electrospray different from the prior studies. Here, flow rate was decreased to 2 $\mu\text{L}/\text{hour}$ due to enhanced solution conductivity. From the scaling law (Equation 1), this predicts a doped droplet size of about half the size of undoped droplet.

Fig. 4: TEM images of gold NPs doped $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ made by electrospray. (a) Dispersion of $\text{Ge}_{23}\text{Sb}_7\text{S}_{70}$ droplets; (b) evidence of a ~ 100 nm diameter droplet containing two gold NPs; (c) higher magnification shows NP size of nominally 5-10 nm

Figure 4 shows the TEM image of several isolated droplets residue from the short (5 second) deposition of gold nanoparticle suspension. The high resolution TEM pictures clearly show the 10 nm NPs are embedded in the glass matrix without aggregation. The improved image contrast of gold NPs and the surrounding ChG matrix confirms the good dispersion of NPs using electrospray. This result supports the notion that the results shown in Fig.1b are more likely due to the poor image contrast instead of ineffective dispersion of the QDs.

3.4 Luminescence studies of CdSe/ZnS QD-doped films

In the case of the core-shell CdSe/ZnS QDs tested in parallel, strong PL was observed from the QDs dispersed in ethanolamine-based solutions. Figure 5 shows PL spectra of CdSe/ZnS QDs in various forms obtained using the Ocean Optics QE Pro-FL instrument.

Fig. 5: Normalized PL spectra of CdSe/ZnS QDs in various environments tested with Ocean Optics QE Pro-FL instrument using two different excitation sources

The PL spectra of these samples are very similar to the data provided by the manufacturer. In these experiments, the signal from the solutions was very strong, such that orange luminescence could be easily seen visibly when either excitation source was directed at the samples. In the case of the QDs in the electrospayed film, the PL signal was also detected under green laser excitation, albeit with low intensity due to the small overall number of QDs in the volume of the thin films interacting with the excitation source. This apparent response from the electrospayed film looks very similar to the response of the pure QDs drop casted on a substrate [30]. The observed blue-shift is believed to be emission from the QDs in the film through modification of the band structure due to the capping agents and matrix [50]. The steady-state spectra are centered at ~600 nm, consistent with the measurements from the other two systems. The time-resolved emission decay is presented in Figure 6. The luminescence decay was fitted with two exponentials 0.26 ns (80%) and 1 ns (20%) with averaged lifetime of 0.63 ns. This value is significantly shorter than the life time (25 ns) of the same QDs dispersed in chloroform [30]. The

electrosprayed film has a decay time significantly shorter than that of QDs in chloroform. This is not surprising as chloroform is a non-quenching environment, while the glass matrix is visible-absorbing and contains residual amines that suggests certain electronic energy transfer from the visible-emitting QD to the matrix may occur.

Fig. 6: Luminescence decay of CdSe/ZnS QD-doped electrosprayed film (black), $\lambda_{\text{ex}} = 532$ nm, $\lambda_{\text{obs}} = 600$ nm; and two-exponential fit (red).

4. Conclusions

We have demonstrated the feasibility of processing QD-doped ChG glass solutions into thin films with good QD dispersion, using an electrospray deposition method. Our findings show that electrospray is not only compatible with ChG solutions, but by determination of solution dopant concentration levels and deposition conditions, one can disperse 10 nm gold NPs and 5 nm QDs effectively without aggregation. The good dispersion is attributed to the isolation of an individual QD in one droplet as defined by the solution preparation, combined with the viscous barrier to aggregation caused by rapid viscosity rise due to fast evaporation that results from the ES deposition condition and choice of solvent. The QDs doped film prepared by electrospray maintain the signature absorption spectra as the manufacturer specifications of QDs. The photoluminescence spectra of electrosprayed thin film of ChG glass doped with QDs shows that

the QD emission is comparable to that reported by the manufacturer. The feasibility of using electrospray to create QDs doped films suggests this method can harness several unique advantages brought by electrospray, which include programmable deposition or printing, 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 for scale up.

Acknowledgments

We thank Dr. Manashi Nath's group at Missouri Science and Technology for preparing the CdTe QDs, as well as Prof. Romain Gaume (UCF) for his help with PL measurements. This work is supported by the Defense Threat and Reduction Agency under contract number HDTRA1-10-1-0101 and National Science Foundation under award numbers CMMI 1301099 and CMMI 1454406.

References

1. V. Hamel, J. Fick, É. J. Knystautas, R. Vallée, A. Villeneuve, F. Schiettekatte, S. Roorda, C. Lopez, and K. A. Richardson, "Photoluminescence in rare-earth-doped chalcogenide thin films," *Optical Amplifiers and Their Applications*, A. Mecozzi, M. Shimizu, and J. Zyskind, eds., Vol. 44 of *OSA Trends in Optics and Photonics (Optical Society of America, 2000)*, paper OMD6.
2. E. N. Borisov, V. B. Smirnov, A. Tverjanovich, and Yu. S. Tveryanovich, "Deposition of Er³⁺ doped chalcogenide glass films by excimer laser ablation," *J. Non-Cryst. Solids* 326–327, 316–319 (2003).
3. V. Lyubin, M. Klebanov, B. Sfez, and B. Ashkinadze, "Photoluminescence and photodarkening effect in erbiumdoped chalcogenide glassy films," *Mater. Lett.* 58(11), 1706–1708 (2004).
4. P. K. Dwivedi, Y. W. Sun, Y. Y. Tsui, D. Tonchev, M. Munzar, K. Koughia, C. J. Haugen, R. G. DeCorby, J. N. McMullin, and S. O. Kasap, "Rare-earth doped chalcogenide thin films fabricated by pulsed laser deposition," *Appl. Surf. Sci.* 248(1-4), 376–380 (2005).
5. V. Lyubin, M. Klebanov, B. Sfez, M. Veinger, R. Dror, and I. Lyubina, "Photoluminescence, photostructural transformations and photoinduced anisotropy in rare-earth-doped chalcogenide glassy films," *J. Non-Cryst. Solids* 352(9-20), 1599–1601 (2006).

6. K. Yan, R. Wang, K. Vu, S. Madden, K. Belay, R. Elliman, and B. Luther-Davies, "Photoluminescence in Erdoped Ge-As-Se chalcogenide thin films," *Opt. Mater. Express* 2(9), 1270–1277 (2012).
7. J. D. Musgraves, N. Carlie, J. Hu, L. Petit, A. Agarwal, L. C. Kimerling and K. A. Richardson, "Comparison of the optical, thermal and structural properties of Ge-Sb-S thin films deposited using thermal evaporation and pulsed laser deposition techniques," *Acta Materialia*, 59 [12] 5032-5039 (2011).
8. E. A. Fagen and H. Fritzsche, "Electrical conductivity of amorphous chalcogenide alloy films," *J. Non Cryst. Solids*, 2 170-9 (1970).
9. G. C. Chern and I. Lauks, "Spin-coated amorphous chalcogenide films," *J. Appl. Phys.*, 53 [10] 6979-82 (1982).
10. D. Bera, L. Qian, T.-K. Tseng, and P. H. Holloway, "Quantum dots and their multi-modal applications: a review," *Materials* 3(4), 2260–2345 (2010).
11. L. Bakueva, S. Musikhin, M. A. Hines, T.-W. F. Chang, M. Tzolov, G. D. Scholes, and E. H. Sargent, "Sizetunable infrared (1000–1600 nm) electroluminescence from PbS quantum dot nanocrystals in a semiconducting polymer," *Appl. Phys. Lett.* 82(17), 2895–2898 (2003).
12. J. M. Pietryga, R. D. Schaller, D. Werder, M. H. Stewart, V. I. Klimov, and J. A. Hollingsworth, "Pushing the band gap envelope: mid-infrared emitting colloidal PbSe quantum dots," *J. Am. Chem. Soc.* 126(38), 11752–11753 (2004).
13. W. Heiss, E. Kaufmann, M. Böberl, T. Schwarzl, G. Springholz, G. Hesser, F. Schäffler, K. Koike, H. Harada, M. Yano, R. Leitsmann, L. E. Ramos, and F. Bechstedt, "Highly luminescent nanocrystal quantum dots fabricated by lattice-type mismatched epitaxy," *Physica E* 35(2), 241–245 (2006).
14. M. V. Kovalenko, R. D. Schaller, D. Jarzab, M. A. Loi, and D. V. Talapin, "Inorganically functionalized PbS-CdS colloidal nanocrystals: integration into amorphous chalcogenide glass and luminescent properties," *J. Am. Chem. Soc.* 134(5), 2457–2460 (2012).
15. R. S. Silva, O. Baffa, F. Chen, S. A. Lourenco and N. O. Dantas, "Luminescence in semimagnetic Pb_{1-x}Mn_xSe quantum dots grown in a glass host: Radiative and nonradiative emission processes," *Chemical Physics Letters*, 567 23-6 (2013).
16. S. El-Rabaie, T. A. Taha and A. A. Higazy, "Characterization and growth of lead telluride quantum dots doped novel fluorogermanate glass matrix," *Materials Science in Semiconductor Processing*, 30 631-635 (2015).
17. S. El-Rabaie, T. A. Taha and A. A. Higazy, "PbTe quantum dots formation in a novel germanate glass," *J. Alloys Compounds*, 594 102-106 (2014).

18. F. Pang, X. Sun, H. Guo, J. Yan, J. Wang, X. Zeng, Z. Chen and T. Wang, "A PbS quantum dots fiber amplifier excited by evanescent wave," *Optics Express*, 18 [13] 14024-30 (2010).
19. C. Liu, Y. K. Kwon and J. Heo, "Absorption and photoluminescence of PbS QDs in glasses," *J. Non Cryst. Solids*, 355 [37-42] 1880-1883 (2009).
20. A. M. Malyarevich, K. V. Yumashev and A. A. Lipovskii, "Semiconductor-doped glass saturable absorbers for near-infrared solid-state lasers," *J. Appl. Phys.*, 103 [8] 081301-1 (2008).
21. K. Wundke, S. Pötting, J. Auxier, A. Schülzgen, N. Peyghambarian and N. F. Borrelli, "PbS quantum-dot-doped glasses for ultrashort-pulse generation," *Appl. Phys. Lett.*, 76 [1] 10-12 (2000).
22. P. Bajaj, E. Woodruff and J. T. Moore, "Synthesis of PbSe/SiO₂ and PbTe/SiO₂ nanocomposites using the sol-gel process," *Mater. Chem. Phys.*, 123 [2-3] 581-584 (2010).
23. A. Sashchiuk, E. Lifshitz, R. Reisfeld, T. Saraidarov, M. Zelner and A. Willenz, "Optical and conductivity properties of PbS nanocrystals in amorphous zirconia sol-gel films," *J. Sol Gel Sci. Technol.*, 24 [1] 31-38 (2002).
24. A. Martucci, P. Innocenzi, J. Fick and J. D. Mackenzie, "Zirconia-ormosil films doped with PbS quantum dots," *J. Non Cryst. Solids*, 244 [1] 55-62 (1999).
25. N. N. Parvathy, A. V. Rao and G. M. Pajonk, "Effects of temperature and sol-gel parameters on PbS crystallite sizes and their spectral and physical properties in a porous silica matrix," *J. Non Cryst. Solids*, 241 [2-3] 79-90 (1998).
26. J. M. Pietryga, R. D. Schaller, D. Werder, M. H. Stewart, V. I. Klimov and J. A. Hollingsworth, "Pushing the band gap envelope: Mid-infrared emitting colloidal PbSe quantum dots," *J. Am. Chem. Soc.*, 126 [38] 11752-11753 (2004).
27. Tver'yanovich, "Concentration Quenching of Luminescence of Rare-Earth Ions in Chalcogenide Glasses," *Y.S. Glass Physics and Chemistry* (2003) 29: 166.
28. C. Lu et al, "Fabrication of uniformly dispersed nanoparticle-doped chalcogenide glass," *Applied Physics Letters*, 105, 261906 (2014).
29. M. V. Kovalenko, R. D. Schaller, D. Jarzab, M. A. Loi and D. V. Talapin, "Inorganically functionalized PbS-CdS colloidal nanocrystals: Integration into amorphous chalcogenide glass and luminescent properties," *J. Am. Chem. Soc.*, 134 [5] 2457-2460 (2012).
30. S. Novak, L. Scarpantonio, J. Novak, M. Dai Pre, A. Martucci, J. D. Musgraves, N. D. McClenaghan and K. Richardson, "Incorporation of luminescent CdSe/ZnS core-shell quantum dots and PbS quantum dots into solution-derived chalcogenide glass films," *Optical Materials Express*, 3 [6] 729-738 (2013).

31. N. Patel, S. Geyer, J. Scherer, M. Bawendi, N. Carlie, J. D. Musgraves, K. Richardson, J. Hu, P. T. Lin, P. Becla, C. Dimas, A. Agarwal, and L. Kimerling, "Infrared Colloidal Quantum Dot Chalcogenide Films for Integrated Light Sources," in *Advanced Photonics, OSA Technical Digest (CD)* (Optical Society of America, 2011), paper IWG3.
32. Patel, Neil Sunil, "Understanding defects in germanium and silicon for optoelectronic energy conversion," Massachusetts Institute of Technology, Date Issued: 2016.
33. S. Novak, D. E. Johnston, C. Li, W. Deng, K. Richardson, "Deposition of Ge₂₃Sb₇S₇₀ chalcogenide glass films by electrospray," *Thin Solid Films* 588 (2015) 56-60.
34. M. Cloupeau, B. Prunet-Foch, "Electrohydrodynamic spraying functioning modes: a critical review," *J. Aerosol Sci.* 25 (1994) 1021.
35. A. Jaworek, "Electrospray droplet sources for thin film deposition," *J. Mater. Sci.* 42 (2007) 266.
36. D.J. Carswell, H.J. Milsted, "A new method for the preparation of thin films of radioactive material of thin films of radioactive material," *J. Nucl. Energy* 4 (1957) 51.
37. K.L. Choy, B. Su, "Titanium dioxide anatase thin films produced by electrostatic spray assisted vapor deposition (ESAVD) technique," *J. Mater. Sci. Lett.* 12 (1999) 943.
38. B. Su, K.L. Choy, "Electrostatic assisted aerosol jet deposition of CdS, CdSe and ZnS thin films," *Thin Solid Films* 361-2 (2000) 102.
39. T. Zhu, C. Li, W. Yang, X. Zhao, X. Wang, C. Tang, B. Mi, Z. Gao, W. Huang, W. Deng, "Electrospray dense suspensions of TiO₂ nanoparticles for dye sensitized solar cells," *Aerosol Sci. Technol.* 47 (2013) 1302.
40. J. Ju, Y. Yamagata, T. Higuchi, "Thin-film fabrication method for organic light-emitting diodes using electrospray deposition," *Adv. Mater.* 21 (2009) 4343.
41. W. Hwang, G. Xin, M. Cho, S.M. Cho, H. Chae, "Electrospray deposition of polymer thin films for organic light-emitting diodes," *Nanoscale Res. Lett.* 7 (2012) 52.
42. T. Fukuda, T. Suzuki, R. Kobayashi, Z. Honda, N. Kamata, "Organic photoconductive device fabricated by electrospray deposition method," *Thin Solid Films* 518 (2009) 575.
43. X.-Y. Zhao, X. Wang, S.L. Lim, D. Qi, R. Wang, Z. Gao, B. Mi, Z.-K. Chen, W. Deng, "Enhancement of the performance of organic solar cells by electrospray deposition with optimal solvent system," *Sol. Energy Mater. Sol. Cells* 121 (2014) 119.
44. Deng, C.M. Waits, B. Morgan, and A. Gomez, "Compact multiplexing of monodisperse electrosprays," *Journal of Aerosol Science* 40, 907-918, 2009.

45. Deng, J. Klemic, X. Li, M. Reed and A. Gomez, "Increase of electrospray throughput using multiplexed microfabricated sources for the generation of monodisperse Droplets," *Journal of Aerosol Science* 37, 696-714, 2006.
46. Hongxu Duan, Cheng Li, Weiwei Yang, Brandon Lojewski, Linan An and Weiwei Deng, "Near-field Electrospray Microprinting of Polymer-Derived Ceramics", *Journal of Micro-electro-mechanical Systems* VOL. 22, NO. 1, FEBRUARY 2013.
47. L. Petit, N. Carlie, F. Adamietz, M. Couzi, V. Rodriguez, and K. C. Richardson, "Correlation between physical, optical and structural properties of sulfide glasses in the system Ge-Sb-S," *Mater. Chem. Phys.* 97(1), 64–70 (2006).
48. Novak, S., Lin, P. T., Li, C., Borodinov, N., Han, Z., Monmeyran, C., et al. "Electrospray Deposition of Uniform Thickness Ge₂₃Sb₇S₇₀ and As₄₀S₆₀ Chalcogenide Glass Films," *J. Vis. Exp.* (114), e54379, doi:10.3791/54379 (2016).
49. A.M. Gañán-Calvo, J. Dávila, A. Barrero, "Current and droplet size in the electrospraying of liquids. Scaling laws," *Journal of Aerosol Science*, Volume 28, Issue 2, March 1997, Pages 249-275.
50. K. Kang and K. Daneshvar, "Matrix and thermal effects on photoluminescence from PbS quantum dots," *J. Appl. Phys.* 95(9), 4747–4751 (2004)