



Effect of nanofiber/thin-film multilayers on the optical properties of thulium-doped silica-alumina

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ABSTRACT

Hybrid layer of Tm^{3+} -doped $\text{SiO}_2\text{-Al}_2\text{O}_3$ nanofiber/thin-film demonstrates broad spectral width with notable high emission intensity. This multilayer structure comprised of thin film sandwiched between two nanofiber-layers, and was prepared via sol gel dip coating and electrospinning techniques, respectively. The emission spectrum achieved more than 5-fold enhancement at 680-nm wavelength and about 51-nm spectral-width, as compared to the emission from a thin film layer. The emitted spectrum peaked at shorter wavelength by about 30 nm from the spectral peak intensity of thin film. The manifestation of the nanostructured layers, which alters the energy levels of Tm^{3+} due to confinement of the ions in low dimensional structure combined with the effect from thin film, resulted in the spectral broadening and increased of spectral intensity. The order of depositing the nanofiber/thin film layers affects the luminescence intensity and peak spectrum wavelength. Thus, tailoring the order in which these layers are to be deposited allows a particular emission characteristic to be achieved.

1. Introduction

Unique and fascinating properties of low dimensional structures (i.e. nanowires, nanotubes, nanorods, nanofiber, nanoparticles, etc.) have gain tremendous attention and have attracted researchers to embark into more extensive experimental and modelling studies on the optical, electronics and magnetic properties. These low dimensional structures have significant advantages over macroscale structures such as high surface area to volume ratio and high porosity, which are useful for wide range of applications such as display, laser, sensor, catalyst, etc. [1,2]. Among these nanostructures, nanofiber have been extensively studied due to their large surface area per unit mass, easy and inexpensive fabrication process. The surface area to volume ratio of the nanofiber is estimated approximately one to two orders of magnitude compared to the thin film [3].

RE acts as active ion in solid-state luminescent materials, allowing them to absorb and emit light at different wavelengths. Incorporation of rare earth (RE) ions in nanostructured host material is of interest because of their sharp emission lines due to their electronic transition in the $4f^n$ band [4–6]. Interaction of RE ions energy levels with electronic states of the host material in nanostructure form may provide unique and efficient luminescence characteristic that would benefits several applications such as laser, solid-state lighting, imaging, display, etc. Silica (SiO_2) glass is an excellent host for RE ions due to its high optical quality, good chemical stability, strong thermal resistance, inexpensive

and high transparency up to 2 μm wavelength [7]. High concentration of RE ion is needed to attain high emission intensity. However, due to the rigid structure of the glass and insufficient number of non-bridging oxygen, highly doped of the RE ions tend to cluster. This ion clustering leads to quenching effect, which eventually reduce the emission efficiency as well as the performance of the device [6].

Various approaches have been carried out to enhance the emission intensity of the active ions such as by co-doping [8], utilizing low phonon host material [9,10], etc. One of the most common techniques to increase the emission intensity in RE-doped glass is to add alumina (Al_2O_3), which exhibits moderate phonon energy ($\sim 870 \text{ cm}^{-1}$). A study by Nogami and Abe in 1996 reported that incorporation of 1 mol % of Al_2O_3 to Eu^{2+} -doped 99SiO_2 has enhanced white emission 250 times stronger compared to the 100SiO_2 [11]. Meanwhile, a study by Monteil et al. in 2004 has found that the Al_2O_3 enhanced the emission of the RE ions through local modification of the RE environment rather than preventing ion clustering [12]. Further study has discovered that the RE ions are found to preferentially located at aluminium-rich domains [13].

Incorporation of the RE ions into a glass nanostructure would be interesting as they could enhance or modify the optical properties that may benefit for various applications. Intense visible light emission is crucial for light source application in order to obtain high brightness. Furthermore, having enhanced and broaden luminescence characteristic would beneficial for lasers and amplifiers for photonics integrated

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circuit.

There are several techniques of depositing RE-doped active layers on a substrate such as sol-gel [14], rf-sputtering [15], atomic layer deposition [16], ion exchange [17], etc. The sol-gel method is an effective method to combine with both dip-coating for thin film and electrospinning for nanofiber that the final properties such as size, composition, thickness, porosity, etc. of the fabricated samples can be prepared as desired [18]. The electrospinning has been proved as a simple, efficient and inexpensive technique to produce nanofiber. By varying electrospinning parameter or modifying setup, nanofiber with different shape or morphology such as ribbon, beaded, porous and core-shell fibers can be obtained [19–21].

In the present work, we report on a relatively simple approach to enhance luminescence intensity by exploiting advantageous properties of the nanofiber containing thulium (Tm^{3+}) active ions in $\text{SiO}_2\text{-Al}_2\text{O}_3$ glass system. Tm^{3+} is one of the attractive RE ions due to its emission spectra at several wavelengths across the visible and infrared wavelength regions [22]. Spectroscopic properties of nanofiber/thin-film multilayers are discussed.

2. Methodology

2.1. Preparation of Tm^{3+} -doped $\text{SiO}_2\text{-Al}_2\text{O}_3$ and PVA solution

Silica (SiO_2) solution was prepared by mixing TEOS with H_2O , HCl and EtOH with the molar ratio 1: 0.01: 2: 37.9 (TEOS: HCl: H_2O : EtOH) [23]. HCl and EtOH were act as catalyst and solvent, respectively. $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ was dissolved in EtOH and then added to the SiO_2 solution with aqueous $\text{TmCl}_3\cdot 6\text{H}_2\text{O}$. The molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 90/10 (mol%) and the doping concentration of Tm^{3+} was 0.8 mol%. The resultant mixture was magnetically stirred at 400 rpm for 16 h at room temperature in order to get homogeneous and transparent solution. A spinnable solution for electrospinning was prepared by combining 6.75 ml of Tm^{3+} -doped $\text{SiO}_2\text{-Al}_2\text{O}_3$ solution to 8.25 ml of polyvinyl alcohol (PVA) at 10 wt%. The solution was stirred at 60 °C for one hour and aged for two days to reach appropriate viscosity that suitable for electrospinning. The coating of the multilayer structure involves two routes, which are the dip coating of thin film (TF) and electrospinning of nanofiber (NF). Deposition of single, double and triple alternate layers of thin film and nanofiber formed hybrid multilayer structures.

2.2. Thin film and nanofiber depositions

A single layer thin film comprised of stacks of 25 nano-scale layers. The nano-scale layers were produced from KSV dip coater, programmed to coat at a dipping rate of 40 mm/min. Each nano-scale layer was annealed at 900 °C for 50 s to remove OH residues and to avoid cracking of the resultant film while maintaining the amorphous structure of the glass [24]. With the coating of the final nano-layer, the thin film was then annealed for 30 min at 950 °C to obtain full film densification. Custom-made horizontal-electrospinning machine was used for nanofiber production. The electrospun nanofiber was heat-treated to remove unwanted organic and hydroxyl compounds; (i) slow ramp rate of 5 °C/min up to 950 °C (ii) maintained temperature at 950 °C for an hour (iii) ramped down the temperature at the rate of 10 °C/min. Three pairs of different layered-samples were prepared and the nomenclature is described as single layer TF and NF; dual-layer TF-NF* and NF-TF*; and triple layer TF-NF-TF* and NF-TF-NF*, where the layer with asterisk (*) indicates that the coating is on the upper most layer. Fig. 1 depicts the schematic diagrams of the multilayer structures. The schematics of dual-layer NF-TF* and TF-NF* structures are not shown here, as they can be visualized from Fig. 1(c) and (d) without the third top layer.

2.3. Characterization

The morphology of the fabricated samples and the ions distribution were examined from field emission scanning electron microscopy (FESEM) imaging and energy disperse spectroscopy (EDS), respectively. The diameters of the electrospun nanofiber were measured using Image J software. Photoluminescent (PL) spectra were measured at room temperature via PerkinElmer LS 55 fluorescence spectrometer under 350 nm excitation. Optical transparencies of the samples were measured in the UV–VIS–NIR wavelength range using Cary 500 Spectrophotometer.

3. Results and discussion

3.1. Surface morphology, average diameter of the fiber and ion distribution

Single layer thin film (TF) and nanofiber (NF) were deposited separately on fused silica substrates. Multilayer TF and NF were deposited in a sequential order for dual-layer TF-NF* and NF-TF*, and triple-layer TF-NF-TF* and NF-TF-NF*. The TF-NF-TF* layers were resulted from depositing TF as the first layer on fused silica substrate, followed by NF as the second layer and then TF* as the third and final top layer. The NF-TF-NF* layers were deposited in same manner with nanofiber on the top layer. Fig. 2 shows surface morphology of the heat-treated samples at 5 kX magnification. The top thin film layers in Fig. 2(a) and (c) show smooth and homogeneous surface without any trace of nanofiber. The electrospun nanofiber top layers, shown in Fig. 2(b) and (d) were able to retain the unbroken long fiber lengths, with random fiber orientation. The fibrous texture of the nanofiber possessed relatively smooth surface after 950 °C of careful heat treatment as demonstrated in Fig. 3 with magnification of 15 kX.

Most of the fibers remain continuous and retain the fibrous structure after heat treatment, which suggests good thermal and mechanical properties of the fibers. Previous study has reported that low thermal treatment rate maintains the fibrous structure and promotes better mechanical properties of the nanofiber [25]. For multilayer structures with TF on the top layer, the appearance of the fibrous morphology of the nanofiber (middle layer) is absence, indicating part of the solution was impregnated into the whole nanofiber layer during the process. Fig. 4 shows the enlarged cross-section image of the NF-TF-NF* sample, which shows the presence of multilayers structure consisting of thin film in between two layers of the nanofiber.

Diameter of fibers are in the range of 122–255 nm for NF and 90–220 nm for NF-TF-NF* structures that were heat-treated at 950 °C for one hour. High temperature of the thermal treatment promotes larger shrinkage of the nanofiber diameter, which resulted from the decomposition of the solvent and organic components of the PVA during the treatment process [26]. Histogram presented in Fig. 5 demonstrates random distribution of nanofiber diameters, though these samples were prepared under similar electrospinning setting parameters and thermal treatment conditions.

The inconsistency of the average diameter distribution and the branching of the nanofiber might either be originated from multijet generated from the solution droplet [27] or electrical bending instability that caused unstable jet trajectory towards the metal collector [20,28]. Furthermore, the ambient conditions such as humidity and temperature could also be the contribution to the inconsistency of fiber diameter. Fig. 6 presents energy dispersed spectrum (EDS), which shows the presence of Si, O, Al and Tm elements in the NF-TF-NF* structure after the heat treatment process, indicating that PVA polymer was fully removed. The presence of C and intense Au peaks were originated from the carbon tape and gold coating, respectively prior to the FESEM-EDS measurement. Fig. 7 shows EDS mapping of these individual ions over the scanned area and it can be seen that all the ions were homogeneously distributed within the host matrix.

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