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Tellurite glass thin films on silica and polymer using UV (193 nm) pulsed laser ablation

Zhanxiang Zhao¹, Gin Jose^{1*}, Paul Steenson², Nikos Bamiedakis³, Richard V Penty³, Ian H White³ and Animesh Jha^{1*}

¹ The Institute for Material Research, Houldsworth Building, Clarendon Road, The University of Leeds, Leeds, LS2 9JT, UK a.jha@leeds.ac.uk and g.jose@leeds.ac.uk

² The School of Electronic and Electrical Engineering University of Leeds, Leeds, LS2 9JT, UK

³Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge, CB3 0FA, UK

Abstract

Erbium doped tellurite glass thin films were deposited using excimer (193 nm) laser ablation onto two different types of substrates: silica and polymer-coated silica for engineering optical integrated active-passive devices. The deposition conditions were optimized for both substrates in order to produce high quality rare-earth (Er³⁺) ion doped glass thin films with low propagation loss. The optical and spectroscopic properties of the deposited films, namely transmittance, fluorescence, lifetime as well as refractive indices at 633 nm were measured and analyzed in detail.

Key words: *Tellurite glass, pulsed laser deposition (PLD), thin films, siloxane polymer, PDMS*

* Corresponding author

1. Introduction

Siloxane polymers are promising materials for passive optical device engineering for applications in optical communication systems due to their high optical transparency and low Rayleigh scattering in the 800-1500 nm wavelength range [1]. These materials exhibit excellent thermal and mechanical properties [2], and over the last 20 years siloxane polymers have been specially engineered for low transmission loss passive and active optical devices, with a range of molecular and physical properties making them structurally compatibility with inorganic substrates. The key passive applications of components fabricated using such films are add/drop multiplexers in arrayed waveguide grating (AWG) geometries, and signal splitters for multichannel transmission with the main active application being thermo-optic and electro-optic switching [3]. The present siloxane polymers exhibit low loss in waveguide structures ($<0.1 \text{ dB cm}^{-1}$) at the common communication wavelengths of 840 nm, 1310 nm, and 1530-1620 nm, and have recently been demonstrated in athermal AWG devices that meet the Telecordia specifications [3, 4].

Siloxane polymer waveguides also have the potential for use in the backplane of personal computers (PC) in the data communication circuits. In high-speed data communication systems operating around 840 nm and in optical communication networks (1310 nm and 1530-1620 nm), the attenuation of signal power can be quite significant due to coupling losses, linear and polarization related losses, and the diffraction loss in AWGs. This means that the multi-wavelength signals must be amplified for optimum performance, requiring active functionality in the polymer based integrated devices. One of the limitations of siloxane and related polymer structures in integrated optical devices at present is their reliance on fluorescent dye molecules for light amplification to compensate the loss of signal power. **The dye molecules when incorporated in polymer matrix have the disadvantage of fluorescence quenching making it impossible to produce continuous wave (CW) gain.** Moreover, the dye molecules age with laser irradiation and, consequently, the amplification process suffers adversely, reducing the lifetime of the component. However, the authors are studying a possible alternative, where, in place of the dye molecules for light amplification, a combined hybrid rare-earth ion-doped glass structure and polymer is used. In this respect the work discussed herein builds upon that of others, such as Pun and coworkers, who studied $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped polymers for amplifying gain medium engineering[5]. Quang et al. employed an erbium doped complex in a polymer matrix for increasing doping concentrations [6], **and Yang et.al recently demonstrated a waveguide amplifier using Nd^{3+} ions doped polymer complex material [7].** **The main objective of the work presented in this paper is to provide an alternative route to light amplification in polymer waveguides, via the integration of the polymer and rare-earth doped glass thin films.**

TeO_2 glasses exhibit large solubility for rare-earth ions [8], which is why this glass host was chosen for forming the thin films. The glass host is also amenable to femtosecond pulsed laser deposition, as originally demonstrated by Jose and co-workers [9]. **Presently however, there are no reported results for**

the PLD deposition of rare-earth doped thin films, or patterned glass waveguide fabrication, on siloxane polymer coated silica substrates, and this is the motivation for the work reported here. Such doped glass structures incorporated on polymers will be a suitable gain block in a polymer-glass integrated device.

The glass thin films were prepared using 193 nm pulsed laser deposition (PLD), which preserves the stoichiometry of the deposited films, compared to that of the source glass. The PLD approach also favors high deposition rates (Hz to kHz pulse repetition rate) and composite/multi-target / material deposition, compared with other common thin film fabrication techniques [10]. The Er^{3+} -ion doped tellurite glass films were fabricated on both silica and polymer coated silica substrates, and the deposition parameters were optimized for both substrates. Subsequently, the thin films were characterized for their optical and spectroscopic properties.

2. Experiments

In this work, tellurite tungsten lanathanum (TWL) glass targets were the source material for the PLD system. The composition of these targets was optimised for this fabrication process and consists, in weight percent (wt%) of 60- TeO_2 , 20- WO_3 , (20-x)- La_2O_3 , where x is weight percentage of Er_2O_3 . Although the value of X can be increased significantly to several wt% , in this work, the percentage of Er_2O_3 was limited to 1 wt% to minimize the effects of concentration quenching and ion-ion cross-relaxations in the Er^{3+} -ion waveguide structures. All precursor chemicals were better than 99.998% pure whereas the purity of rare-earth oxides was limited to only 99.99%. The constituent oxides were mixed and ground using a mortar and pestle inside a dry glove box and then transferred into an alumina crucible, which was then placed inside a muffle furnace maintained at 975°C. The crucible was held at 975°C for 2.5 hours in a dry oxygen atmosphere with the flow rate of 1L/min for melting and homogeneization purposes. Subsequently, the melt was cast into a polished bronze mould preheated at 400°C. The quenched liquid formed glass which was then left to anneal at 430°C for 3 hrs, after which it was allowed to cool down to room temperature at a rate of 0.5 °C/min. The high melting temperature of the glass do not favour the use of gold crucible, while a platinum crucible undergo corrosion on melting the glass with chemical composition reported above.

The glass samples prepared were polished and their thermal properties were studied using differential thermal analysis (DTA). The results showed that the T_g and T_x of the glass were 438 °C and 610°C, respectively, which indicates that the glass has excellent thermal properties.

The prepared target was mounted in the target holder inside a custom-built pulsed laser deposition chamber, equipped with a 193 nm excimer with 20 ns pulse duration source. The substrate material was placed vertically above the target with a separation of 50 mm. The pulsed laser was focused on the target with the fluence of 1.3 J/cm² and a repetition rate of 10 Hz. Prior to deposition the PLD chamber was

pumped down to less than 10^{-6} mTorr, and then filled with high purity process gases (O_2 or 96% O_2 :4%He) at a rate of 20 sccm, whilst continuing to pump in order to maintain a residual pressure of 135 mTorr. During the deposition experiments, a range of temperatures between room temperature and 400°C were tried. However, for the active-passive waveguide integration with siloxane polymer coated silica substrate, we focused on two temperature limits: one at 100°C, which is close to the glass transition temperature (T_g) of polydimethyl siloxane (PDMS), and the other at 300°C, above which the polymer degradation due to thermal decomposition becomes significant. The thickness of the siloxane layer on silica was $\sim 25\mu\text{m}$. Since the T_g of the TWL glasses are in the range of 420°C to 450°C, and for better structural compatibility and stress management between the three dissimilar materials (PDMS, TWL, and the silica substrate) the higher substrate temperature for the film deposition was considered preferable, in the first instance, which is why we chose to start with a 300°C.

The transmittance and fluorescence of the TWL-PLD films were measured with an Ultraviolet-visible-NIR spectrometer, Lambda 19 (Perkin Elmer) and a Spectro-fluorimeter (Model FS 920, from Edinburgh Instruments, UK) respectively, while a Metricon prism coupler (model 2010) was employed for measuring the refractive index, thickness and propagation loss of the films at 633 nm. The compositions of the bulk glasses and the thin films were investigated using energy dispersive X-ray analysis (EDX) and the XRD. The surface topography of the deposited films was examined using a LEO 1530 field-emission-scanning electron microscope (FEG SEM). All these measurements were repeated after three months of preparing and the results were remained unchanged showing stability of the structures for such durations.

3. Results and discussion

The compositions of the target glass and the thin films obtained using EDX are listed in table 1 in atomic%. The EDX data of the samples show 2.71 atomic% aluminum (~ 0.7 mol% Al_2O_3) introduced in the target glass due to the use of an alumina crucible for glass melting. Varying concentrations of Al are present in the thin films reported in the table. Being a glass former, the presence of Al_2O_3 in such small concentrations will not detrimentally affect the optical and spectroscopic properties of the glass. The XRD of the target glass and thin films prepared under different conditions are reported in figure 1 show no sharp peaks resulting from crystalline phase and confirms the amorphous nature of the material.

Table 1 The compositions of target and thin films in atomic% measured using EDX

Element/Glass thin films deposited on	O	Te	W	La	Er	Al
Silica substrate at 100°C in O ₂	87.3	6.0	3.4	1.4	0.2	1.7
Silica substrate at 300°C in O ₂	80.2	7.5	8.1	2.7	0.1	1.4
PDMS on silica substrate at 100°C in O ₂	83.8	7.6	5.8	2.3	0.2	0.3
PDMS on silica substrate at 100°C in 96vol%O ₂ /4vol%He	81.6	7.7	6.2	2.4	0.2	1.9
Bulk glass	78.4	11.7	3.7	3.1	0.3	2.7

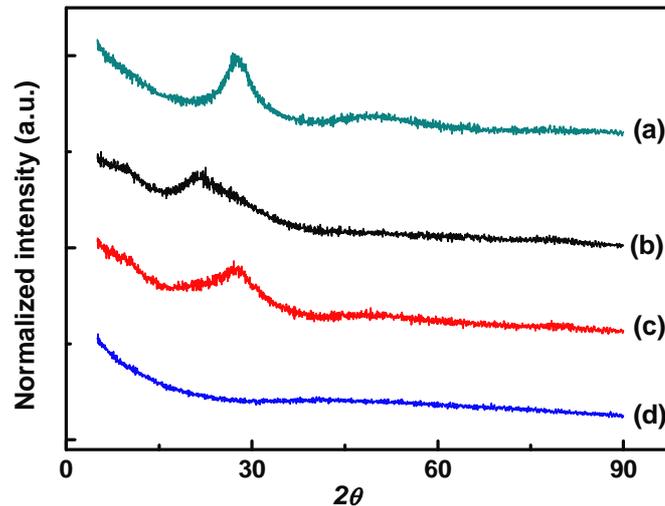


Figure 1. XRD of samples: (a) target glass, (b) glass film on silica deposited at 100°C, (c) glass film on silica deposited at 300°C and (d) glass film on polymer deposited at 100°C

3.1 Optical properties and topography of thin films on silica substrates

All transmittance measurements were measured using a double beam spectrophotometer with bare silica substrate as reference. As shown in figure 2, the transmittance of the thin film deposited at 100°C on the silica substrate was as high as 95%, over the range of 650 nm to 2500 nm. By comparison, the transmittance of the thin films deposited at 300°C, despite having lower thickness, is seen to be fractionally lower than those fabricated at 100°C, which is the result of smaller particle clusters

constituting the film at higher substrate temperature (see figure 3). The interference fringe patterns shown in figure 2 are an indication of thickness uniformity of the films in the measured area.

Figures 3a and 3b show the SEM images of the surface of the films deposited at 100 °C and 300 °C respectively. It is apparent that there is no much difference in the film structure, except the nano-scale grain boundaries (dark appearance in the image) per unit area. The particle size on average is much smaller and there is no cracks shown for the 300°C deposition while at 100°C there is better agglomeration of particles of relatively larger size and fewer cracks at the nanoscale. The comparison of microstructure also confirms the reformation and growth of particulates in the post-plasma plume, which carries a majority of ablated materials through kinetic energy exchange with the gas molecules to the substrate. In addition, several samples has been prepared at 100 °C and 300 °C respectively using exactly the same deposition parameters, and the results showed that the topography and optical properties of the thin films deposited at the same conditions were reproducible.

The refractive indices and propagation loss of the thin films deposited at 100°C on silica substrates were measured at 633 nm using the prism coupler, and were found to be 1.80 and 0.2 dB/cm, respectively. While the thin films deposited at 300°C have a higher refractive index of 1.920 and an optical loss of 0.7 dB/cm. The distinction of refractive index between these two thin films indicates difference density of the thin films [11]. While the difference in loss values observed for two films can be justified by the different refractive index contrast between the thin film and the adjoining silica substrate, and the nanoscale defects on the surface shown in figure 3a, that affect the Rayleigh scattering losses [12-14].

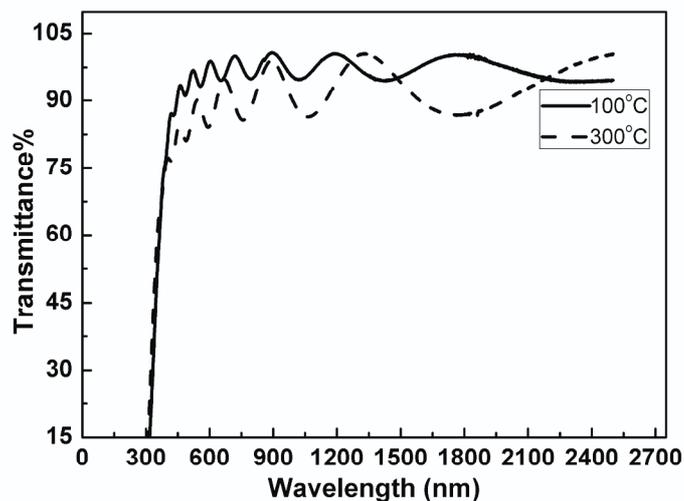


Figure 2: Optical transmittance spectra of the TWL glass thin films deposited on silica substrates in the UV, visible and NIR range.

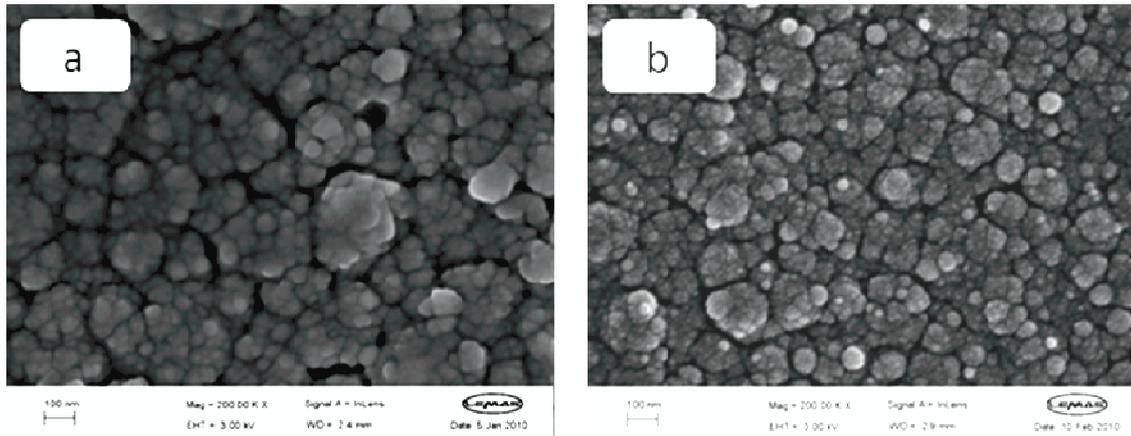


Figure 3: SEM images of a TWL glass thin deposited over silica substrate at (a) 100 °C and (b) 300 °C

In figure 4, the room temperature fluorescence in the Er^{3+} :ion doped TWL glass thin films deposited on the silica substrate at 100°C and 300°C are compared. The spectra were measured using a 980 nm semiconductor diode laser. The pumping at 980 nm excites the $\text{Er}^{3+} : ^4\text{I}_{15/2}$ states to a metastable $^4\text{I}_{11/2}$ state, from which the non-radiative decay occurs and populates the lasing level at $^4\text{I}_{13/2}$. The line-widths of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in TWL thin films deposited on silica substrates at 100°C and 300°C have similar shape, and no significant difference in the peak position. The small blue shift (~ 3 nm) of the peak of the spectrum of high temperature deposited film compare to that of the film deposited at 100°C is within experimental error.

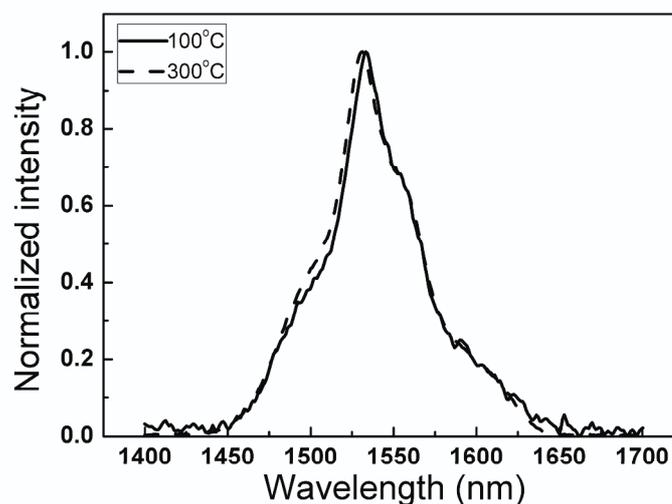


Figure 4: The room temperature PL spectra of the TWL thin films deposited at 100°C (solid) and 300°C (dashed)

The values of the fluorescence bandwidth ($\Delta\lambda = \int Id\lambda / I_{\max}$) of two photoluminescence (PL) spectra are reported in table 2, and the bandwidth of the films deposited at 100°C and 300°C are the same at 72 nm. The lifetimes of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition are also compared as well as the experimental data of the propagation losses, refractive index (at 633 nm) and thickness of the films are listed in table 2. And it can be observed that the PL lifetime of the films deposited on silica is lower compared to that of the target. This can be attributed to larger –OH concentration in the films resulting in increase of the nonradiative relaxation from ${}^4I_{13/2}$ level. The origin of these hydroxyl groups may be from the moisture present in the process gas used during the deposition and the presence of nanoscale grain boundaries also favors moisture adsorption.

Table 2: Optical and spectroscopic properties of TWL bulk glass and thin films deposited on plain and polymer-coated silica substrates

Glass films deposited on	Gas atmosphere for deposition @ 135 mTorr	Refractive index at 633 nm (± 0.0005)	Loss at 633 nm ($\text{dB cm}^{-1} \pm 0.2$)	Fluorescence bandwidth (nm)	Lifetimes (ms) ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ (± 0.02)	Thickness (μm) ($\pm(0.5\% + 5 \text{ nm})$)
Silica substrate at 100°C	O ₂	1.8201	0.2	72	2.28	1.073
Silica substrate at 300°C	O ₂	1.9213	0.7	72	2.00	0.983
PDMS on silica substrate at 100°C	O ₂	1.6380	1.1	69	1.24	1.698
PDMS on silica substrate at 100°C	96 vol% O ₂ -4 vol% He	1.8954	0.1	71	1.22	0.784
Bulk glass	-	2.0965	-	77	5.30	-

3.2 Optical properties and topography of thin films on PDMS coated on silica substrates

In our experiments we confined all the TWL glass on polymer-coated substrates deposition to temperatures below 150°C to avoid polymer decomposition. Although these materials decompose readily between 300 °C-400°C [15], under high vacuum environments, such as the one in the PLD chamber, the degradation of polymer structure can take place at even lower temperatures.

For the deposition of thin films on polymer-coated substrates, two different ambient gases were used in the PLD chamber: high purity oxygen and a mixture of 96 vol % oxygen with 4 vol% of helium. The

reason for introducing helium (He) with O₂ in the chamber at a comparable partial pressure is that the ionization energy of He is higher than that of O₂ (He: 24.59eV and O₂: 13.62 eV), and the high energetic He species (He radical and He ions) has the advantage of reducing the roughness of the thin film surface [16]. In figure 5 the SEM images of TWL glass thin films deposited on the PDMS-coat silica substrate are shown. The thin films prepared in O₂-He atmosphere, shown in figure 5b appear to have much denser and finer structures than that deposited in O₂ atmosphere, as shown in figure 5a.

The microstructures observed in the SEM images in figure 5 significantly differ from those shown in figures 3a and 3b in terms of number of cracks per unit area. The cracks seen in figure 5 appear to have a width below 50 nm but are interconnected to a scale of few hundreds of nanometers. It can be concluded from the deposition experiments that the cracking tendency in TWL glass films on silica and PDMS coated silica is strongly dependent on the thermal expansion coefficient of the substrate property, and less on the substrate temperatures and the types of gases used in the deposition process.

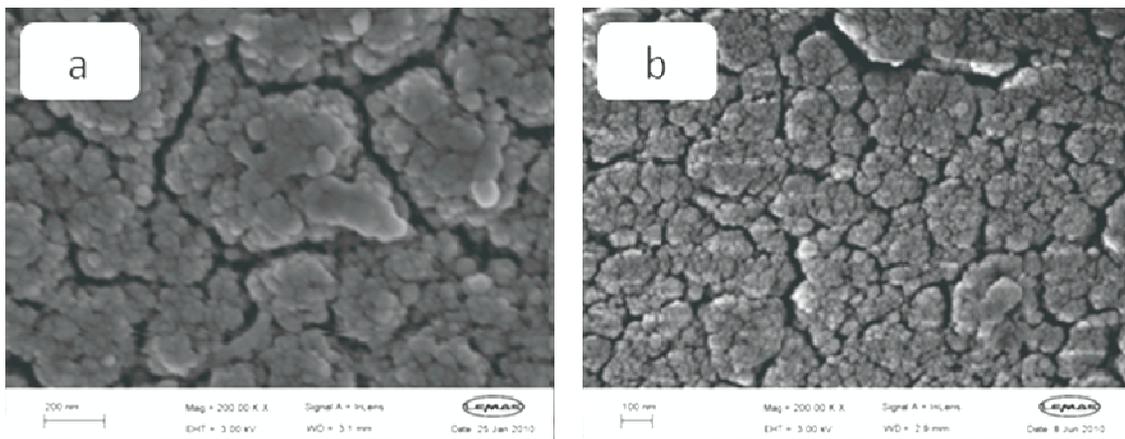


Figure 5: SEM images of TWL glass thin films on polymer substrates: a) at 100°C in O₂ gas, b) at 100°C in a gas mixture of 96 vol% O₂ and 4 vol% He.

The transmission spectra of TWL glass films on PDMS, formed at 100°C in a residual gas of pure oxygen and a mixture of 96 vol% O₂ and 4 vol% He are compared in figure 6. The two films exhibit better than 90% transmittance between 800 nm and 1600 nm. However, the film deposited with He/O₂ mixture shows marginally better transmission at shorter wavelengths below 800 nm.

The measured refractive index and propagation loss at 633 nm for these two films on PDMS-coated silica substrates are compared in table 2. The TWL films deposited on PDMS-coated silica have higher refractive index at 1.89 than the films deposited on plain silica substrates alone at 1.82. Since the index of refraction depends significantly on the material density, the comparison of measured refractive indices of the TWL films with bulk glass indicates a lower density for the TWL glass films which can be attributed

to the fractional porosity in the film due to the presence of nano-scale cracks, shown in figures 3 and figure 5.

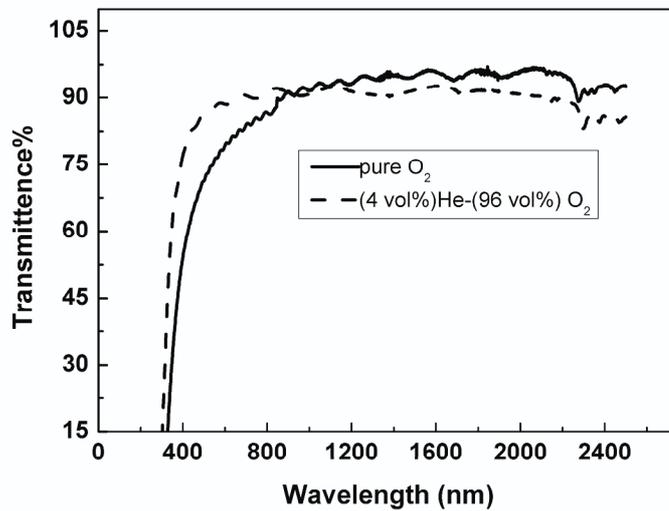


Figure 6: UV-visible-NIR transmittance spectra of the TWL glass thin films deposited in pure oxygen and oxygen/He mixtures on PDMS coated silica substrates

The room temperature photoluminescence spectra of the TWL glass thin films, deposited in oxygen and oxygen-helium mixture are compared in figure 7. The PL spectra, corresponding to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for Er^{3+} -ions present in the TWL glass, indicate that the two films are structurally similar. The deposited film in the presence of O_2/He gas, exhibits comparable PL bandwidth with the film deposited in O_2 atmosphere, which are 71 nm and 69 nm, respectively and there is no apparent shift in the peak positions in figure 7.

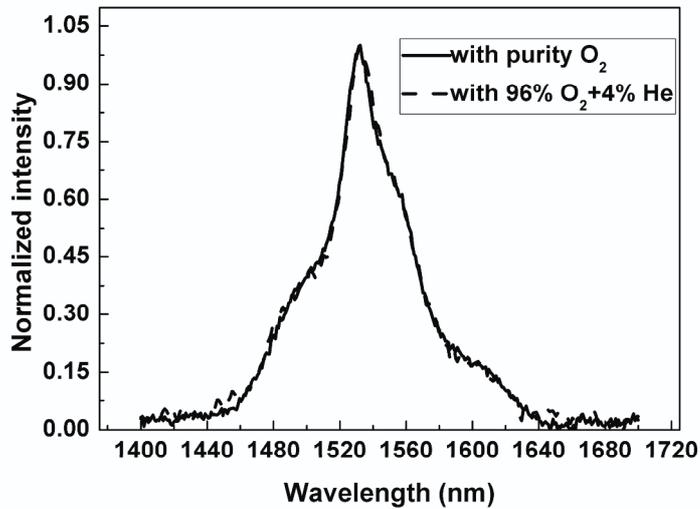


Figure 7: Room temperature PL spectra of TWL glass films, deposited at 100°C on PDMS coated silica substrates in O₂ and O₂/He atmospheres.

As shown in table 2, the lifetime of films on polymer have a further reduction in the lifetime compare to that of the thin film on silica, and this may be due to the formation of polymer-rare earth complexes at the polymer-glass interface. To confirm the exact origin of the reduction of the transition lifetime observed in the films deposited on two types of substrates, more detailed investigations are required.

Conclusions

High-quality TWL glass thin films were fabricated on plain and polymer-coated silica substrates using PLD. The thin films of TWL glass formed at 100°C have a propagation loss of 0.21 dB/cm while the film on polymer-coated substrate exhibited a lower loss of 0.1 dB/cm. We found from the refractive index measurements that the higher temperature thin films were much denser than that deposited at 100°C. The measured PL bandwidth and lifetimes of Er³⁺: ⁴I_{13/2} to ⁴I_{15/2} transition in the films are smaller than that in the bulk glass. Further optimization of the deposition conditions is required to improve these spectroscopic properties. The PLD method presented in this paper has potential for use for the fabrication of glass -polymer integrated optical devices with both active and passive functionalities.

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