

Luminescence Properties of Low Temperature Sol-Gel Organic-inorganic Hybrid Films Contained Rare-earth Ions

Wenxiu Que, L. Cheng, C.Y. Jia and M. Sun

School of Electronic and Information Engineering, Xi'an Jiaotong University,
28 Xianning Road West, Xi'an 710049, Shaanxi, P. R. China
TEL:86-29-82668679, e-mail: wxque@mail.xjtu.edu.cn.

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Abstract

GeO₂/ormosil organic-inorganic hybrid films doped with neodymium ions and TiO₂/Ormosil organic-inorganic hybrid films dispersed with neodymium oxide nanocrystals are prepared by combining an inverse microemulsion technique and a low-temperature sol-gel technique. The effects of Nd³⁺ concentration, Nd₂O₃ nanocrystal content, and heat treatment temperature on up-conversion and photoluminescence luminescence properties of the hybrid films are studied.

1. Introduction

Recent spectroscopic results have showed that neodymium ion could be used as a good candidate for upconversion fluorescence and lasers [1]. Therefore, there has recently been a considerable amount of interest in the up-conversion process of this ion in various kinds of glass or crystal host materials [2]. Among the up-conversion materials, bulk crystals, glasses, and fibers are quite attractive, but high cost associated with the material preparation and device packaging as well as not integrating with semiconductors may limit their applications. Films, on the other hand, combine the advantages of the bulk materials and the compactness of fibers, offering good prospects for up-conversion devices. Recently, optical ly homogeneous and transparent organic-inorganic hybrids containing organic components have been widely synthesized and reported. The introduction of organic groups into an inorganic network can improve mechanical properties, leading to an easy processing of thick film. Organic-inorganic hybrids are thus anticipated as the desirable materials for photonic applications. Especially, hybrid waveguide in thin film configuration become more important, they can be obtained at a low heat treatment temperature, which would allow directly integrating

on the same chip the active devices with the pump sources, the photodetectors, and other optoelectronic components. Therefore, it is of great interest and significance to study the planar hybrid waveguides doped with neodymium ions or other rare-earth ions for photonic applications.

We report on preparation, planar waveguide, and upconversion luminescence properties of GeO₂/γ-glycidoxypolytrimethoxysilane (GLYMO) organic-inorganic hybrid films doped with Nd³⁺-ions and TiO₂/GLYMO organic-inorganic hybrid films dispersed with neodymium oxide nanocrystals. The effects of Nd³⁺ concentration, Nd₂O₃ content, and heat treatment temperature on upconversion luminescence and photoluminescence properties of the hybrid films are also investigated. The mechanism responsible for the enhancement of the violet, blue, and UV emissions is discussed.

2. Experimental

The neodymium oxide nanocrystals were prepared by the microemulsion technique [3] and then those were thoroughly dispersed in TiO₂/GLYMO matrix by using a Vortex mixer to form the nanocrystals in this matrix. It should be mentioned that TiO₂/GLYMO was employed as matrix, which was expected to provide good mechanical and optical properties, conferring high kinetic stability on nanometer-sized compound particles. Especially, a dense thick film at low heat treatment temperature was obtained through the TiO₂/GLYMO material system. In the preparation of the TiO₂/GLYMO sol, 1 mole GLYMO was mixed with 4-mole ethanol and 4 mole de-ionized water, and the mixture was stirred for about 30 minutes. Tetrapropyl orthotitanate was chelated with an acetyl acetone in molar ratio 1:4 in nitrogen environment and the

solution was agitated for obtaining homogenization. Two solutions were then mixed based on a required molar ratio. The final mixture was stirred for about 30 h at room temperature. Spin-coating was performed to deposit the hybrid films with an agitated sol. We used silicon as substrates and they were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with the de-ionized water and dried in pure N₂ gas. Each single layer of the sol-gel film was spun onto the substrate at 4000 rpm for 35 seconds. Then, the coated film was directly put in the furnace and heated at different temperatures. Similarly, Nd³⁺-doped GeO₂/GLYMO hybrid waveguide films were prepared by a sol-gel technique in an organic-inorganic system. Germanium isopropoxide and neodymium nitrate (Nd(NO₃)₃·6H₂O) were used as the precursors of GeO₂ and Nd³⁺, respectively. The details of the preparation processing of GeO₂/GLYMO hybrid material system were described in Reference [4]. Neodymium was added as neodymium nitrate with a Nd/(GeO₂+GLYMO) molar concentration of 0.5 mol. % drop-by-drop into the GeO₂/GLYMO hybrid solution. The final mixture was stirred for about 50 h at room temperature.

The up-conversion emission spectra were measured with a yellow light at the wavelength of 577 nm on a Spex Fluorolog-3 spectrofluorometer, attached with a 1934D3 phosphorimeter. This system employs the Datamax software package for acquiring the spectra and the decay curves. The source of excitation is a Xe-cw source for the steady state up-conversion emission measurement and a Xe-flash lamp was used for the lifetime measurements. Photoluminescence (PL) were excited with an Ar⁺ laser at 514 nm having an output power of 200 mW and mechanically chopped at 80 Hz. The PL emission from the hybrid thin film was collected by two lenses, dispersed through an ORIEL (model 77200) monochromator and detected with an ORIEL (model 71905) detector and channeled to a lock-in amplifier for intensity recording. In order to remove the excitation wavelength, a long pass filter was placed in front of the monochromator.

3. Results and discussion

Figure 1 shows visible up-conversion emission characteristic spectrum of radiation emanating from the hybrid thin film dispersed with neodymium oxide nanocrystals under the excitation of 587 nm. The absorption spectrum of the hybrid thin film revealing an excitation transition of neodymium ion

(Nd³⁺) at 587 nm ($^4I_{9/2} \rightarrow ^4G_{5/2}$) was shown in the inset of Fig.1. The reason behind the selection of this wavelength is that the neodymium ions have intense absorption transition ($^4I_{9/2} \rightarrow ^4G_{5/2}$) at 587 nm band and hence it was chosen to measure the up-conversion emission spectrum of the hybrid thin film dispersed with neodymium oxide nanocrystals. It can be seen from Fig.1 that apart from a bright violet up-conversion emission at 402 nm corresponding to the $^4D_{3/2} \rightarrow ^4I_{13/2}$ or $^2P_{3/2} \rightarrow ^4I_{11/2}$ transitions of the neodymium ions, an ultraviolet emission transition at 372 nm ($^4D_{3/2} \rightarrow ^4I_{11/2}$ or $^2P_{3/2} \rightarrow ^4I_{9/2}$) and a blue emission transition at 468 nm ($^4D_{3/2} \rightarrow ^4I_{15/2}$ or $^2P_{3/2} \rightarrow ^4I_{13/2}$) have also been observed. But it should be noted that the ultraviolet emission at about 345 nm hasn't been observed, and the peak positions of other emissions have been found a little shift because of the energy transfer as compared with the emission spectrum of neodymium oxide nanocrystals. This might be due to the effect of the host material. It should be mentioned here that our up-conversion luminescence transition spectrum of $^4D_{3/2} \rightarrow ^4I_{J+1}$ or $^2P_{3/2} \rightarrow ^4I_J$ ($J=13/2, 11/2, 9/2$) was found to be essentially similar as those reported in Refs.[5,6]. Especially, except the slight red shift of the emission position, the spectrum of our hybrid thin film is almost identical to that reported in Ref.[7]. It should be also mentioned that this is the first observation of the intense up-conversion luminescence at 402 nm from the neodymium (III) ion in a hybrid thin film heated at low temperature of 100°C as a result of being induced by a continue-wavelength xenon lamp.

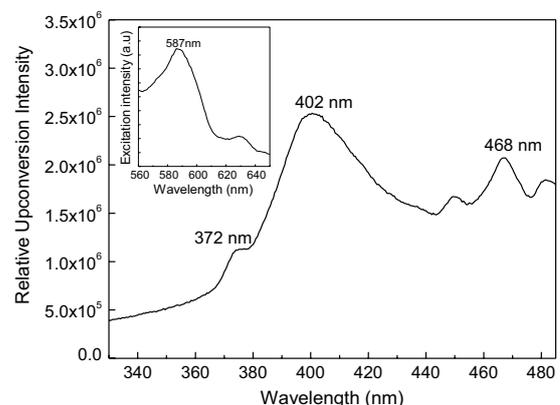


Fig.1. Visible up-conversion emission spectrum from the hybrid thin film heated at 100°C under the excitation of 587 nm.

The decay time of the up-conversion violet emission at 402 nm of the hybrid thin film was obtained and the result showed that the lifetime of the hybrid film is relative short at around 12 μ s. Above results and analysis indicate that the up-conversion mechanism in our films includes the sequence of ground- and excited-state absorption steps [8]. Simply, the observed up-conversion emission in Figure 1 is due to sequential two-photon absorption process. Figure 2 provides the schematic diagram to explain the mechanism of up-conversion emission from a neodymium ion via a two-photon absorption process.

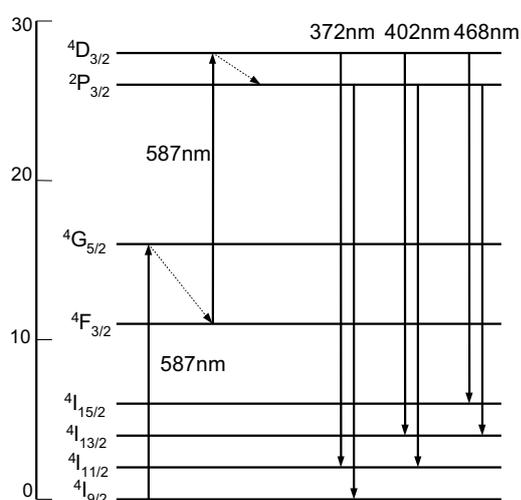


Fig. 2. Energy level scheme describing the up-conversion emission from the composite thin film upon excitation at 587 nm.

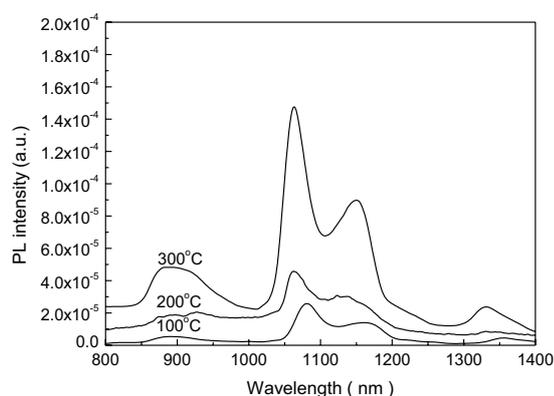


Fig. 3. PL spectra of TiO₂/GLYMO hybrid thin films dispersed with Nd₂O₃ nanocrystals as a function of baking temperature.

Figure 3 shows the photoluminescence emission spectra at room temperature as a function of heat treatment temperature from the neodymium oxide nanocrystals dispersed in TiO₂/GLYMO hybrid thin films. It could be seen that an emission spectral main peak centered at 1.064 μ m was observed in these samples heated at 200 and 300 $^{\circ}$ C, which is associated with the intra-4*f* transition corresponding to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition of the neodymium (III) ion. It could be noticed from Fig.3 that the peak intensity has increased a lot with an increase in the heat treatment. However, the peak position of the Nd³⁺ emission have hardly been changed with an increase in the heat treatment for the thin films at the temperatures of 200 and 300 $^{\circ}$ C. The increasing of the peak intensities could probably be due to the organic solvents becoming completely decomposed and hence relatively dense thin films were gradually formed with the increase of the heat treatment temperature. It should be mentioned that there is no obvious peak intensity change when the films heated between 100 $^{\circ}$ C and 200 $^{\circ}$ C. We suppose that the relatively weak PL intensity of these composite thin films is probably due to the incomplete evaporation of water and volatilization and thermal decomposition of the remnant organic solvents. It is also noted that there is an interesting shift of 8 nm with this lasing transition at 1064 nm for common neodymium-doped glasses whereas at 1072 nm for our composite thin film heated at 100 $^{\circ}$ C. This shift can be attributed to the fact that the emission depends considerably on the host matrix, which is due to the water and the remnant of organic solvents. In addition, the shoulder at about 1145 nm was observed in the films heated at different temperatures and this shoulder peak reaches a maximum intensity after a heat treatment temperature of 300 $^{\circ}$ C. It should be mentioned that this shoulder peak was not observed in the previously reported neodymium doped materials. The mechanism of this emission has not been clear, but we suppose that it could probably be due to TiO₂/GLYMO matrix. In order to prove this assumption, the TiO₂/GLYMO matrix and neodymium oxide nanocrystals were measured separately to confirm their luminescence characteristics. Figure 4 shows the PL emission spectra at room temperature of the TiO₂/GLYMO hybrid films as a function of heat treatment temperature. It could be seen from Fig. 4 that the luminescence band at 1145 nm is clearly observed in all measured samples and the peak intensity changes a lot with the heat treatment temperature. In addition to above mentioned emission peak at 1.064 μ m or 1.072 μ m in

Fig.8. Two other measured near infrared luminescence bands at 890 nm and 1336 nm, which are assigned to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions respectively, were also observed for the film heated 300°C.

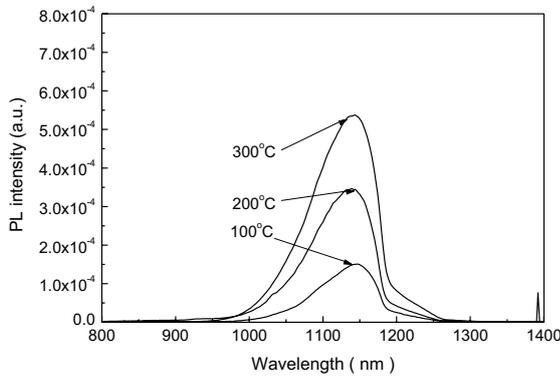


Fig. 4. PL spectra of TiO₂/GLYMO hybrid thin films as a function of baking temperature.

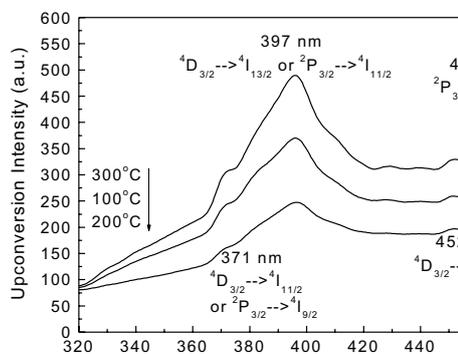


Fig. 5. visible up-conversion emission spectra from the GeO₂/GLYMO hybrid film doped with a 0.5 mol% neodymium content and heated at different heat treatment temperatures.

Figure 5 shows the up-conversion emission spectra of the 0.5 mol% Nd³⁺-doped two-layer GeO₂/GLYMO hybrid films heated at different heat treatment temperatures under the excitation of 584 nm. The spectra illustrate clearly that the up-conversion emission intensity of the hybrid film changes a lot with the heat treatment temperature. However, the

peak position and the shape of the spectra are independent of the heat treatment temperature. The up-conversion emission intensity of the hybrid film heated at 300°C is the highest of all the films measured. There are no reasonable reasons explaining why the emission intensity of the film is relative weak when the heat treatment temperature is at 200°C. We suspect that it is probably due to the incomplete decomposition of the organic solvents in the hybrid films at the heat treatment temperature of 200°C.

4. Summary

Nd₂O₃ nanocrystals dispersed in TiO₂/GLYMO composite thin films and Nd³⁺-doped GeO₂/GLYMO hybrid thin films have been prepared. We have measured and analyzed systematically an intense violet up-conversion upon excitation with a yellow light from the Nd³⁺-ions and found that these phosphors are displaying very encouraging violet up-conversion emissions. A relatively strong room temperature NIR emission at 1064 nm has been observed as a function of heating temperatures. The up-conversion mechanism has been proposed due to a two-photon absorption process.

5. References

1. Y. Guyot, H. Manna, J. Y. Rivoire, R. Moncorgé, N. Garnier, E. Descroix, M. Bon, and P. Laporte *Phys. Rev. B*, **51**, 784 (1995).
2. E. L. Falcão-Filho, Cid B. de Araújo, and Y. Messaddeq, *J. Appl. Phys.*, **92**, 3065 (2002).
3. W.X. Que, Y. Zhou, Y. L. Lam, Y. C. Chan, C. H. Kam, L. H. Gan, and G. Roshan Deen, *Mater. Res. Bull.*, **36**, 889 (2001).
4. W. X. Que, X. Hu, and Q. Y. Zhang, *Appl. Phys. B*, **76**, 423 (2003).
5. X. Zhang, C. Serrano, E. Daran, F. Lahoz, G. Laco ste, and A. Muñoz-Yagüe, *Phys. Rev. B*, **62**, 4446 (2000).
6. O. S. Wenger, D. R. Gamelin, H. U. Güdel, A. V. Butashin, and A. A. Kaminskii. *Phys. Rev. B*. **61**, 16 530 (2000).
7. B. Zhou, Y. Zhou, Y. L. Lam, C. Y. Chan, C. H. Kam, S. D. Cheng, and S. Buddhudu, *Opt. Commun.*, **182**, 151 (2000).
8. J. C. Wright, *Top. Appl. Phys.*, **15**, 239 (1976).