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EFFECT OF TEMPERATURE, DOPING CONCENTRATION ON OPTICAL PROPERTIES OF ZnO NANOPARTICLES AND Er^{3+} IONS CO- DOPED SILICA

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Abstract:

This work reports on SiO_2 thin films co-doped with ZnO nanoparticles and Er^{3+} ions prepared by sol- gel method and spin- coating process. After growth, heat treatment processes in the air at the annealing temperatures of 600 ^oC, 700 ^oC, 800 ^oC, 900 ^oC and 1000 ^oC for 3h have been applied for calcination. Scanning electron microscopic images showed that ZnO nanoparticles dispersed in a thin layer of SiO_2 are formed with diameter in the range of about 20-30 nm. The characteristic emission band at 1540 nm from intra-4f electronic shell of Er^{3+} ions can be observed. We found that these PL spectra depend on annealing temperature, Er doping concentration and ZnO content. It can explained by the energy transfer from ZnO nanocrystals to Er^{3+} dopants.

Keywords: *ZnO-SiO_2 nanocomposite, Er^{3+} ions, photoluminescence, energy transfer, thermal quenching.*

I. INTRODUCTION

Erbium (Er)- doped silica materrials have been extensively investigated for application in fiber amplification [1]. The reason for that is the wavelength 1540 nm emission by radiative transition in the intra- 4f electonic shell of trivalent erbium Er^{3+} lying low-loss window (C band) in silica optical fiber. The disadvantages of the Er-doped silica is the small excitation absorption cross- section of Er^{3+} ions [2] and the solubility of Er^{3+} in the silica host matrix is low [3] results in low emission efficiency. Co- doping of the materials is often applied to improve the excitation csoss-section. This includes SiO_2 co- doped with Er^{3+} ions and ZnO nanocrytals. In suchthe case, ZnO nanocrystals are intermediate materials that help to enhanced photoluminescence (PL) intensity of Er^{3+} by a energy transfer process from ZnO nanocrystals to Er^{3+} dopants [4, 5]. Thus, enhance the Er- related PL intesity- with band gaps ~ 3.4 eV at room temperature and a large excitation- binding energy 60 meV [6], ZnO is an idea intermediate material that cam reduce the back transfer process, in is also enviromentally friendly material.

In this work, we report our recent development of sol- gel and spin- coating methods to prepare thin films ZnO- SiO_2: Er^{3+}. The characteristic PL spectra Er^{3+} ions are presented. The effect of temperature, doping concentration on the optical properties of the materials are annalyzed and discussed. The efficient energy transfer from ZnO nanoparticles to Er^{3+} ions involves to efficient PL emission is also observed.

II. EXPERIMENTS

The sol-gel and spin- coating method was used to prepare the ZnO and Er^{3+} co- doped SiO_2 thin films.

A SiO_2 sol was prepared by mixing tetraethylorthosilicate (TEOS) solution with ethanol with ratio 1:1, and pH was adjusted to 2 by adding HNO_3. As prepared solution of a mixture was prehydrolyzed at 70 ^oC for 4 h. Then it was cooled down to room temperature.

A ZnO sol was prepared for the ZnO precusor part, zinc acetate was dissolved in ethanol. For the total dissolution of the acetate, the molar ratio of diethanolamine (DEA), ethanol and zinc acetate was added into the sol $Zn(CH_3COO)_2$: C_2H_5OH : DEA = 1 : 50 : 1. The mixture was stirred at 70 ^oC for 4h and down to temperature.

The ZnO sol was added into the SiO_2 sol slowly and the mixture sol was stirred for another 1h to obtain a homogeneous sol. Then $Er(NO_3)_3.5H_2O$ dissolved in ethanol was added and stirred at room temperature for 20h. the solution was dropped onto Si or SiO_2 subtrates by spin- coating, which were rolated at 2500 rpm for 30 s. After depositing by

spin- coating, the films were anealed at 600 °C for 2 min. Finally, 25- layer films were obtained and the films were anealed from 600 °C to 1000 °C in air for 3 h.

Morphologies of the nanocomposites on the substrates were investigated by FESEM- JEOL JSM-7600F field emission scanning electron microscope (FESEM). Photo emission and excitation spectra were recorded and analyzed by using Horiba Nano Log spectroscopic system. The excitation source utilizes a 450 watt intense broadband continuous wave (cw) xenon lamp for bright excitation from ultra-violet (UV) to near infrared (NIR) in combination with a double-grating monochromator.

III. RESULTS AND DISCUSSION

Figure 1a shows a FESEM image of the sample with ZnO:SiO_2 ratio of 5:95 and 0.3 mol % Er^{3+} co-doped annealed at 700 °C for 3 h. We can see ZnO nanoparticles with size around 20- 30 nm are formed and distributed homogeneously in SiO_2 host matrix. In figure 1b, the thichness of the films is equally and it were the size of about 3.32 µm.

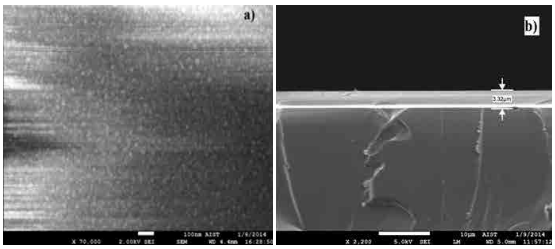

Figure 1. *a) FESEM images of the film with ZnO:SiO_2 composition ratio of 5:95 upon annealing temperature at 700 °C. b) FESEM cross section surface images*

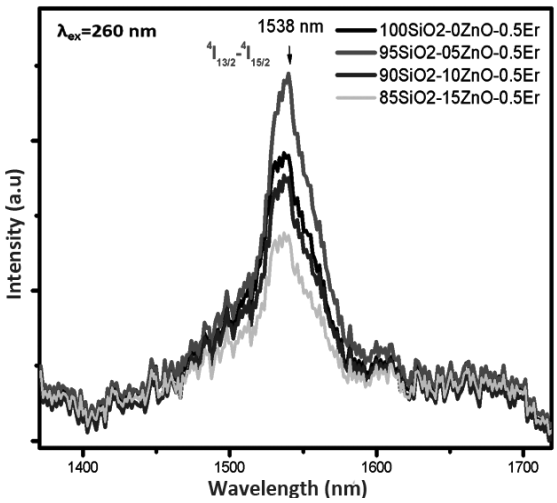

Figure 2. *PL spectra of the films containing 0.5 mol % Er^{3+} with ZnO compositions varied from 0 mol % to 15 mol %*

Figure 2 shows PL spectra of the films containing 0.5 mol % Er^{3+} annealed at 700 °C with different ZnO: SiO_2 molar % ratio of 0:100; 5:95; 10:90 and 15:85, measured at room temperature under excitation wavelength at 260 nm. The characteristic 1538 nm NIR emission due to the transition of $^4I_{13/2} - {}^4I_{15/2}$ from Er^{3+} ions is exhibited corresponding to radiative transitions in the 4f electric shell of Er^{3+} ions [5]. The sample with 5 mol % ZnO gives the highest luminescence intensity.

Figure 3 shows the PLE spectrum monitored at 1538 nm covers a broad band from 255 to 480 nm and a sharp peak at 260 nm which provides convincing evidence that efficient energy transfer from ZnO nanoparticles to Er^{3+} ions has been achieved. Excitation energy is absorbed by the ZnO nanoparticles in host matrix and transmit for the rare earth ions and resonant emission of Er^{3+} ions enhances the emission of these ions. Besides a broad peak at wavelength 380 nm is direct stimulated for the emission band to band of ZnO nanoparticles which enhanced emission of Er^{3+} ions in the 1538 nm wavelength.

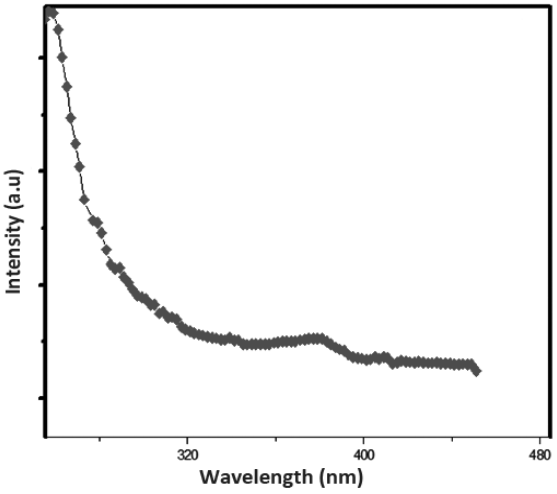

Figure 3. *PLE spectra of the samle 5 %ZnO:95 %SiO_2:0.3% Er^{3+} upon annealing temperature at 700 °C*

Figure 4 shows PL spectra of the thin films with Er^{3+} compositions varied from 0 mol % to 0.7 mol % and ZnO: SiO_2 composition ratio of 5:95 annealed temperature at 700 °C. The thin films with 0.3 % of Er^{3+} ions gives the highest luminescence intensity. When the concentration of Er^{3+} low obtained emission signal is very weak due to the number of luminescent center is poor. The concentration doping increase over 0.3 mol % PL intensity decreases due to the effect concentration quenching [7]. The clusters is formed

and connected with the other clusters to maked more than luminescence center. The energy is tranmitted by intra between the optical centers lead to fluorescence quenching.

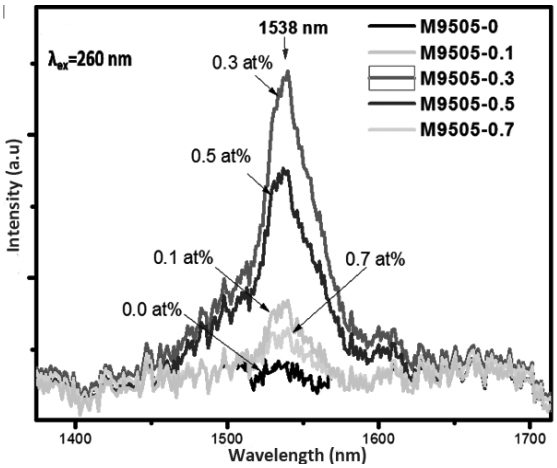

Figure 4. *PL spectra of the sample[8] with range Er^{3+} concentration from 0 mol % to 0.7 mol % and containing 5 mol % ZnO upon annealing temperature of 700 °C*

In Figure 5 shows PL of the thin films were annealed in air at 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C for 3h. PL intensity increase with the annealing temperature raising from 600 oC to 700 °C. It is found that 700 °C annealing results in the strongest band located at 1538 nm. Then PL intensity decrease when temperrature continued to rise to 1000 °C. High temperature annealing may be form Zn-O-Si bonds or Zn_2SiO_4 phase, which is the cause of Er^{3+} PL quenching.

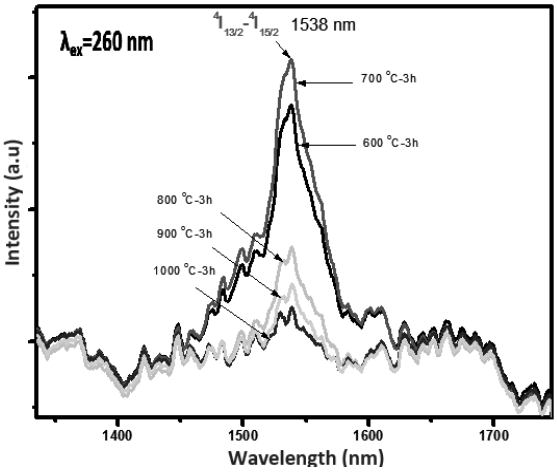

Figure 5. *PL spectra of thin films containg 5 mol % ZnO and 0.3 mol % Er^{3+} ions upon different annealing temperature*

IV. CONCLUSION

SiO_2 thin films co- doped with Er^{3+} ions and ZnO nanoparticles were prepared by sol- gel method and spin- coating process. The morphologies of the samples were obtained by FESEM measurements. The Er^{3+} characteristic emission is enhanced with increasing ZnO concentrations demontrating an effective energy transfer from ZnO nanopartiles to Er^{3+} ions. The PL intensity is higest for the thin films ZnO: SiO_2 with molar ratio 5: 95 doped 0.3 mol % Er^{3+} and annealing temperature at 700 °C.

V. ACKNOWLEDGMENTS

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ẢNH HƯỞNG CỦA NHIỆT ĐỘ, NỒNG ĐỘ PHA TẠP LÊN TÍNH CHẤT QUANG CỦA VẬT LIỆU SILICA ĐỒNG PHA TẠP VỚI TINH THỂ ZnO VÀ ION Er^{3+}

Tóm tắt:

Trong bài báo này chúng tôi trình bày kỹ thuật chế tạo màng mỏng SiO_2 đồng pha tạp với tinh thể ZnO và ion Er^{3+} bằng phương pháp sol- gel kết hợp với kỹ thuật quay phủ. Sau quá trình quay phủ màng mỏng được ủ nhiệt ở các nhiệt độ 600 ^oC, 700 ^oC, 800 ^oC, 900 ^oC và 1000 ^oC trong 3 giờ trong môi trường không khí. Ảnh hiển vi điện tử cho thấy xuất hiện tinh thể ZnO trong ma trận SiO_2 với kích thước cỡ 20-30 nm. Vật liệu cho phát xạ ở vùng bước sóng 1540 nm đây là bước sóng trong lớp 4f của ion nguyên tử Er^{3+}. Chúng tôi thấy rằng phổ huỳnh quang của vật liệu phụ thuộc vào nhiệt độ ủ, nồng độ pha tạp Er và nồng độ ZnO đã được khảo sát. Cơ chế truyền năng lượng từ tinh thể ZnO sang ion Er^{3+} được xác nhận.

Từ khóa: *Nanocomposite ZnO- SiO_2, ion Er^{3+}, huỳnh quang, cơ chế truyền năng lượng, dập tắt huỳnh quang do nhiệt độ.*