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Visible erbium luminescence in Er^{3+}-doped SiO_2–TiO_2 films prepared by sol–gel method

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Er^{3+} doped SiO_2-TiO_2 composite films were prepared by depositing the sols on the Si substrate surface using a spin-coating technique. The effect of annealed temperature and the ratio of Ti/Si on the microstructure and photoluminescence properties of composite films were studied. The structure of the samples was investigated by X-ray diffraction (XRD), and Raman technique. The photoluminescence (PL) spectra were recorded at room temperature. The results showed that the PL intensity was dependent on the annealing temperatures and the ratio of Ti/Si.

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1. Introduction

Lanthanide ion doped nanostructured materials have been studied in the past few years due to a growing interest in their size-dependent physical properties and potential applications in optoelectronic technology [1]. TiO_2 and SiO_2 are widely used materials in optical film filters in the visible and near infrared wavelength range because of their chemical stability and large refractive index difference. SiO_2-TiO_2 mixed oxides have also been studied as catalysts in organic reactions [2] or in selective oxidation reactions [3]. Therefore, TiO_2-SiO_2 composite films have been extensively investigated using different preparation processes, such as sol-gel [4-6], sputtering [7, 8], Atomic Layer Deposition [9], chemical vapor deposition [10], electronic beam evaporation [11]. More recently SiO_2-TiO_2 mixed oxides have been proved to be suitable host matrices for rare earth ions [12-15]. When rare earth elements are included in the films composition, the layers show luminescence properties, which make possible applications such as integrated laser sources or optical amplifiers.

Sol–gel technology is a low temperature method of preparing metal oxide films by a chemical route. The main advantages of sol-gel process over other physical alternatives are a great flexibility in material composition and structure, because of the ease of introducing a wide range of dopants. This method allows preparation of materials with exceptional purity, homogeneity and composition. It can be associated with dip coating or spin coating processes, which are appropriate techniques for a large range of substrate types [16].

The aim of this work is to study the experimental conditions which determine the best Er^{3+} luminescence in SiO_2–TiO_2 thin films. In this paper, the erbium luminescence behavior is discussed in relation to films composition and microstructure. For this purpose, a series of Er^{3+}-doped SiO_2–TiO_2 thin films was fabricated by the sol-gel method. The composite films showed strong photoluminescence, and its emission intensity was a function of the annealed temperature and the ratio of Ti/Si. The crystalline structure of these composite films is presented.

2. Experimental

Er^{3+}-doped SiO_2–TiO_2 thin films were obtained by the sol–gel technique. The samples were prepared by the sol-gel process using tetraethoxysilane (TEOS), ethanol, deionized water, tetra-n-butyl titanate ($Ti(OC_4H_9)_4$), $Er(NO_3)_3 \cdot 5H_2O$ as the starting materials. The Er^{3+} amount relative to total cation concentration (Ti+Si) is 2% for all the samples. The films were prepared in the process involving six stages:

1. TEOS was hydrolyzed with a mixed solution of ethanol and deionized water, followed by stirring for 1h at about 60°C
2. $Ti(OC_4H_9)_4$ was mixed with the ethanol, deionized water, hydrochloric acid, and $Er(NO_3)_3 \cdot 5H_2O$
3. The silica and titanium solutions were mixed together and stirred for 2 h at room temperature yielding the hydrolyzate.
4. Thin films were obtained by spin-coating (3300 rpm) of the sols on Si substrate.
5. The first group of samples was different Ti/Si ratios at 5/1, 2/1, 1/1, 1/5, and 1/10 annealed at 900°C for 1h in air.
6. The second group of samples was annealed at 600, 700, 800, 900, and 1000°C fixed Ti/Si ratios at 5/1 for 1h in air.

2.2 Characterization

X-ray diffraction (XRD) pattern of the samples were obtained with X-ray diffractometry (Rigaku D/Max-ⅢC) using Cu Kα radiation. Raman spectra were measured with a micro-spectrascopy (JY-HR800) using a 532nm Ar^+ ions laser as the exciting light source. PL Spectra were performed on a John Yvon HR800 spectrometer at 325nm. All measurements for the samples were carried out at room temperature.

3. Result and discussion

Fig. 1(a) shows XRD patterns of the samples of 2 mol % Er^{3+} doped with different Ti/Si ratios annealing at 900 °C for 1 h. When the Ti/Si ratio is less than 2, no diffraction peak is detected, the samples show typical amorphous glass pattern. With the increasing of Ti/Si ratio, the crystallization phase appears. The peak for crystallization of TiO_2 in the anatase phase becomes more prominent with increasing Ti/Si ratio. Each peak of TiO_2 is indexed and all of them are assigned to the tetragonal anatase. The peak values of the anatase phase are also in good agreement with the reported values in the literature (JCPDS 21-1272). No additional phase was found and diffraction peaks related to Er^{3+} compound could not be detected, implying that the Er^{3+} ions have been effectively built into the TiO_2/SiO_2 composite films.

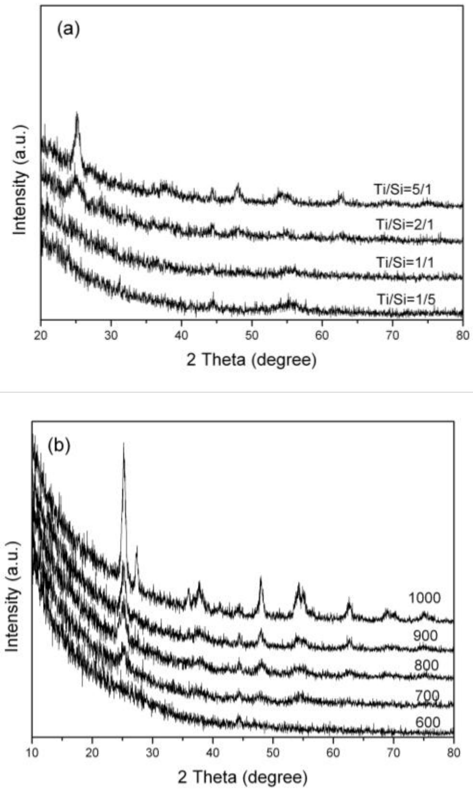

Fig. 1 (a) XRD pattern of the samples of 2 mol% Er^{3+} with different Ti/Si annealing at 900°C for 1h; (b) XRD patterns of the samples $5TiO_2$-SiO_2 prepared at different annealing temperatures (600°C -1000°C).

Fig. 1(b) shows XRD patterns of the samples of 2 mol % Er^{3+} doped $5TiO_2$-SiO_2 prepared at different annealing temperatures (600–1000 °C). It is known that TiO_2 is formed as a stable tetragonal anatase under heat treatment at 700 °C, and a tetragonal rutile structure above 700 °C [17]. In the present study, despite the relatively high heat treatment temperature of 1000 °C, the mixed form of the rutile and anatase structures is observed while the brookite phase is never detected. We can surmise that the formation of TiO_2 rutile structure is prevented by the presence of silica and thus, the phase transition temperature is shifted to a higher temperature region with the higher SiO_2 content in the mixed system. This result suggests that the formation of anatase phase would be extended to higher temperature in SiO_2/TiO_2 composite thin films. The crystallite size can be determined from the XRD pattern according to the Scherrer equation. The crystallite sizes for different annealing temperatures from 700 °C to 1000 °C are estimated as 2.7 nm, 6.9 nm, 10.6 nm, 13.9 nm, respectively. Thus these materials can be seen as nanocomposites where the major part of TiO_2 is embedded in an amorphous silica matrix.

Fig. 2 (a) shows the Raman spectra of 2 mol % Er^{3+}-doped samples with different ratios of Ti/Si annealed at 900°C. There is no Raman peak for the samples with Ti/Si ratio lower than 2. This result is in agreement with the XRD (see Fig.2 (a)). The anatase as crystalline phase was detected for the samples with Ti/Si ratio up to 2. No extra peaks due to another phase, such as rutile, were detected. The result shows that the introduction of SiO_2 inhibited the crystallization of TiO_2 and elevated the phase transition temperature. The peak intensity of the anatase mode in the Raman spectra considerably decreased with increasing SiO_2 content.

The Raman spectroscopy of amorphous silica usually presents a large band at 440 cm^{-1} and weaker bands located at 492 and 605 cm^{-1}. The band at 440 cm^{-1} has been assigned to combinations of the Si-O-Si and O-Si-O bond bending vibrations. The bands at 488 and 605 cm^{-1} have been attributed to defects in the network [18-20]. So the broad band at 550 cm-1 is due to superposition of the crystallization TiO_2 and amorphous SiO_2. From these various data, it can be concluded that the nanocomposite nature of the prepared samples consist of amorphous silica and crystallization TiO_2.

Fig.2 (b) shows the Raman spectra of 2 mol % Er^{3+} doped $5TiO_2$-SiO_2 prepared at different annealing temperature (600-1000 °C). The samples annealed at 600 °C have a certain extent of amorphous phase because its Raman spectra are considerably weaker as compared with other samples. The content of the amorphous phase in the samples is thought to gradually decrease with the increasing annealed temperature, corresponding to the increase in intensity of Raman spectra. With the increasing of Ti/Si ratio, the Raman peak of the E_g mode for the TiO_2 has a red shift due to the strain causing by the surface coating.

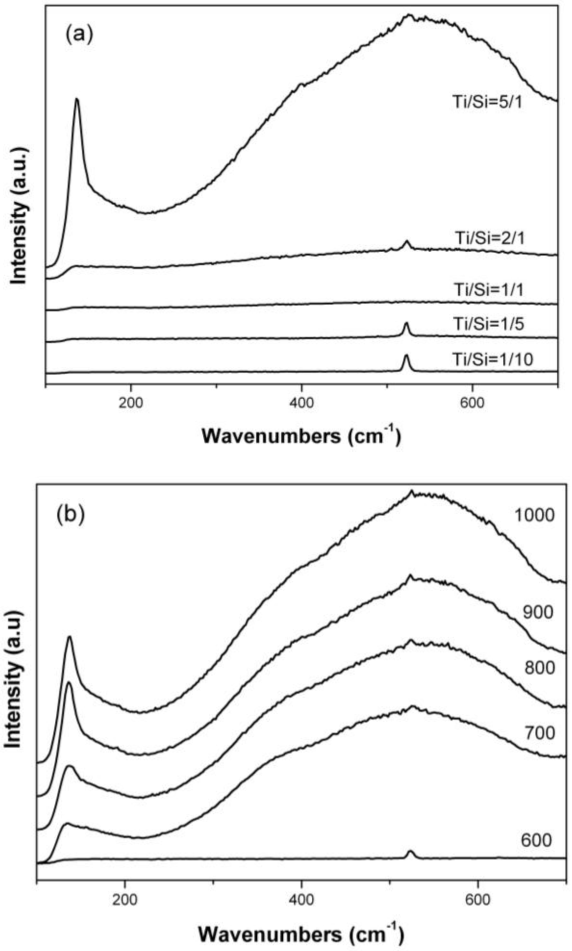

Fig. 2. (a) Raman spectra of the samples 2 mol% Er^{3+} with different Ti/Si annealing at 900°C for 1h; (b) Raman spectra of the samples of 5TiO_2-SiO_2 prepared at different annealing temperatures (600 °C -1000 °C).

The energy level diagram of Er^{3+} ions in the visible range is given in Fig. 3. Radiation at a wavelength of 325 nm led to excitation of the Er^{3+} ions. Intermediate excited states were then populated through non-radiative transition and then depopulated through radiative transition.

Fig.4 (a) shows the PL spectra of the samples with different ratios of Ti/Si annealing at 900 °C for 1h under the excitation of 325 nm He-Cd laser. The luminescence bands, with maxima centered at 520 nm, were assigned to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transition. The bands with maxima located at 560 nm were assigned to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition. The bands with maxima centered at 660 nm were attributed to the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition.

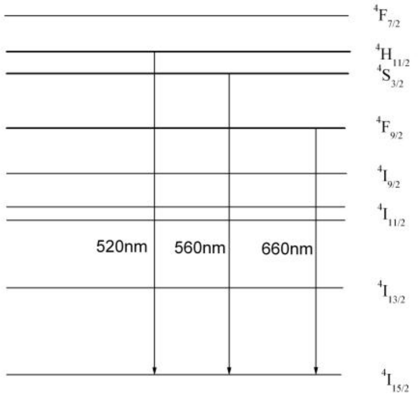

Fig.3 Energy level diagram of Er^{3+} ions in the visible range

An enhancement of the luminescence was observed when increasing the Ti/Si ratio, from 1/10 to 5/1 and a fixed Er^{3+} ions content of 2 mol%, as depicted on Fig. 3 (a). The weakest luminescence intensity corresponds to the lowest Ti/Si ratio, and as Ti/Si ratio increase, the Er^{3+} concentration quenching effect vanishes, enhancing luminescence intensity. This behavior can be explained in terms of the affinity of Er^{3+} to enter in the TiO_2 lattice, thus increasing TiO_2 content the ions get more separated and the interaction among them are less feasible.

Fig.4 (b) shows the PL spectra of 2 mol % Er^{3+} doped 5TiO_2-SiO_2 prepared at different annealing temperature (600-1000 °C) for 1h. The annealed temperature plays an important role in the photoluminescence intensity of Er^{3+} doped 5TiO_2-SiO_2 composite thin films. The intensity of the main emission peak increases with the increasing of annealed temperature from 600 °C to 900 °C, When the annealing temperature is above 900 °C, the decrease in the PL intensity can be observed. This phenomenon is temperature quenching effect. The ionic radius of Er^{3+} (0.89 Å) is much larger than those of the Si^{4+} (0.4 Å) and Ti^{4+} (0.69 Å). As a consequence, the solubility of Er^{3+} in 5TiO_2 –SiO_2 composite thin films is limited. However, even at 1000 °C of annealing, the Er–O–Si (Ti) matrix is in the amorphous state and TiO_2 is partially transformed into rutile phase. So the PL of the above 900 °C of annealing samples could be related to the prestage of aggregates. At the initial stage, the Er^{3+} ions can be relaxed weakly from the O–Si–Ti bonding and increase the effective interaction between the neighboring Er^{3+} ions. Such clustering can increase the probability of the nonradiative of the optically active ions to the ground electronic state. Thus, the clustering process might be responsible for the observed quenching of the PL.

The $^2H_{11/2}\rightarrow{}^4I_{15/2}$ transition is hypersensitive and therefore particularly suitable to detect the change in the environment immediately around the Er^{3+} ions [21]. The crystal-glass transformation around the active ions affects the spectral linewidth and this is observed in this experiment. The crystal-field strength experienced by the optically active ions directly reflects the maximum energy splitting of the Stark components of the electronic level. With the increasing of annealed temperature and the Ti/Si ratio, narrower bands splitted into several lines appear superimposed on the bands at 520 nm, 560 nm, and 660 nm. This splitting has already been reported elsewhere [22] and can be attributed to the transition between the Stark sublevels of the upper states ($^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$) and the ground state $^4I_{15/2}$, due to a crystalline environment of the rare earth. The XRD results indicate that the local environment of the erbium transforms from amorphous to crystalline with the increasing of annealed temperature and the Ti/Si ratio.

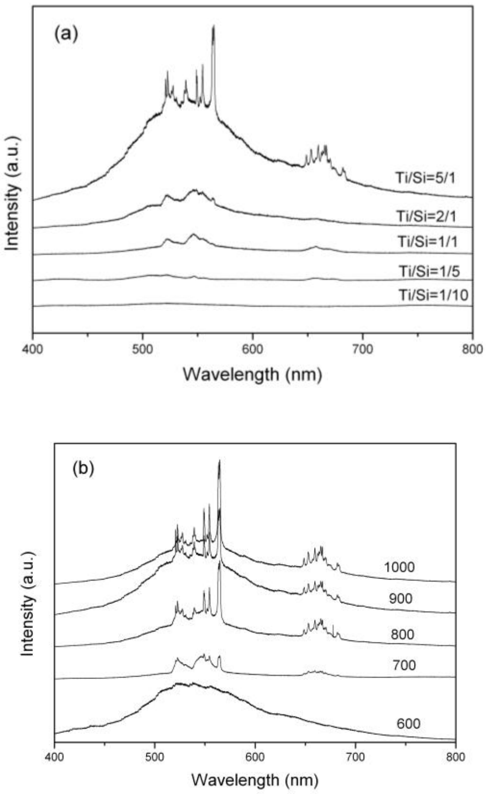

Fig. 4. (a) Photoluminescence spectra of the samples 2 mol% Er^{3+} with different Ti/Si annealing at 900°C for 1h; (b) Photoluminescence spectra of the samples of 5TiO_2-SiO_2 prepared at different annealing temperatures (600°C -1000°C).

As mentioned previously, the radii of the rare earth ions are too large to allow them to replace TiO_2 in an anatase crystal. This fact indicates that the rare earth ions are located at the edge of the nanocrystallites, or in close proximity to these surface defects. There are a great number of the surface states available to transfer energy to the crystal field states of the rare earth ions due to the small size and large number of nanocrystallites in these materials. The energy level of these surface defects is critical to the energy transfer process because if it is lower in energy than the emitting state of the rare earth ion, no sensitized luminescence can be observed. When Er^{3+} ions were doped in TiO_2-SiO_2 host, since the energy for visible emission of TiO_2 was higher than the energy of intra-4f transition of Er^{3+} ions [23, 24]. The excitation energy could be nonradiatively transferred to Er^{3+} ions, enhancing its characteristic emission.

4. Conclusion

Er^{3+} doped TiO_2-SiO_2 composite films were deposited on Si substrates by sol-gel method with spin-coating technique. The XRD and Raman results showed that the crystalline phase of composite SiO_2-TiO_2 films was strongly affected by the ratio of Ti/Si and annealing temperature. PL spectra, measured at room temperature, showed a strong visible luminescence corresponding to $^4S_{3/2}$→$^4I_{15/2}$ transition at ~ 560 nm. The intensity of luminescence was affected by the annealing temperature and the ratio of Ti/Si.

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