Structural characteristics, luminescent properties and energy transfer processes of CeO₂:Er³⁺ thin films

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Abstract CeO₂:Er³⁺ films were deposited by electron-beam evaporation technique. Photoluminescence properties of Er³⁺ doped CeO₂ films annealed in air atmosphere were investigated. Visible and near-infrared emission peaks were assigned to the transitions from ²H_{11/2}, ⁴S_{3/2}, ⁴F_{9/2}, ⁴I_{11/2} and ⁴I_{13/2} levels to ⁴I_{15/2} level, respectively. The structure and the luminescent properties of CeO₂:Er³⁺ films were characterized by X-ray diffraction, photoluminescence and photoluminescence excitation spectra. In addition, luminescence intensities of Er³⁺ and the intensity ratio of red/green emission peaks were also investigated. They were strong affected by the doping concentration of Er³⁺. With the good luminescent properties, CeO₂:Er³⁺ films should be promising candidates for multifunctional applications.

Keywords: Thin film; CeO₂:Er³⁺; Photoluminescence; Energy transfer

1. Introduction

Rare earth ions doped materials have attracted great attention for several past years, owing to the irreplaceable role in eye safe visible and near-infrared (NIR) lasers, silicon based optoelectronic integration, biomedical diagnostics, optical amplifiers and many other applications[1-5]. Specially, much attention has been paid to the

trivalent erbium ion (Er^{3+}) due to its unique radiative transitions in the visible and NIR region. Er^{3+} exhibits green ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) emission bands in the visible region, which has been extensively studied for laser applications[6]. Meanwhile, the NIR emission around 1.54 μm , which is attributed to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition, falls within the low-loss band of silica-based optical fibers[7, 8].

Nevertheless, the common disadvantage of mostly rare earth is the extremely low absorption coefficient. This difficulty can be solved by selecting a suitable host material. Cerium dioxide (CeO_2) is known for its cubic fluorite structure, high dielectric constant (~ 26)[9] and excellent chemical stability. It has been widely used in optical and optoelectronic devices due to the high transparency in visible and NIR region[10]. And it has a unique feature that Ce^{4+} and Ce^{3+} in CeO_2 can be converted to one another[11, 12]. Additionally, CeO_2 has low phonon cutoff energy (465 cm^{-1}) and high solubility with other rare earth ions. These properties make it suitable for practical application and become ideal host materials for Er^{3+} . Therefore, Er^{3+} doped CeO_2 film is a kind of promising material.

In this paper, $\text{CeO}_2:\text{Er}^{3+}$ films were deposited on Si wafers by electron-beam evaporation technique. We report the observation of visible and NIR emission from Er^{3+} doped CeO_2 films that were annealed in oxygen atmosphere. The structure of $\text{CeO}_2:\text{Er}^{3+}$ films were analyzed by X-ray diffraction (XRD), and the luminescent properties were analyzed by photoluminescence (PL) and photoluminescence excitation (PLE) spectra. Furthermore, the effects of Er^{3+} doping concentration on luminescence intensity and intensity ratio were also investigated, as well as the optimal doping concentration of Er^{3+} . These results will contribute to the investigation of Er^{3+} activated luminescent materials.

2. Experimental

The $\text{CeO}_2/\text{Er}_2\text{O}_3$ multilayer films with different concentration were deposited by EVA450 type e-beam evaporation equipment on silicon (100) wafers. The Si substrates were cleaned by Radio Corporation of America (RCA) process. Then the films were deposited in the high-vacuum chamber with the pressure of $9 \times 10^{-5} \text{ Pa}$, and

high-purity CeO₂ (99.99%) and Er₂O₃ (99.99%) were used as starting materials. The thickness of CeO₂ layer was kept constant (200 nm) and films were consisted with different Er³⁺ concentration of 0.5 at.%, 1 at.%, 5 at.%, 10 at.% by varying the thickness of Er₂O₃ layer. The obtained films were annealed at 1050°C for 1h in air.

The crystal structures of annealed films were identified by XRD using an X-ray diffractometer (Bruker D8 Advance). The PL and PLE spectra were measured with a fluorescence spectrometer (FLS920) using 450W Xenon lamp as a light source and a photomultiplier (190-870 nm) along with a liquid nitrogen cooled Ge (800-1700 nm) as the detectors.

3. Results and discussion

Fig. 1a shows XRD patterns of the CeO₂:Er³⁺ films at various Er³⁺ doping concentration. All the films possess the CeO₂ (111) cubic phase and no sharp characteristic peak of Er₂O₃ is evidenced, indicating that Er³⁺ ions have diffused into the host lattice. The crystallite size of the films was determined from XRD by Scherrer's formula and the calculation made on diffraction line (111) with an obvious variance. The crystallite size of the films decreased with increasing concentration. The trend interprets that the crystallization of films decrease by the increase of Er³⁺ doping. The enlarged (111) peaks near 28.5° of the CeO₂:Er³⁺ films at various Er³⁺ doping concentration are shown in Fig. 1b. It can be seen that the XRD peaks of Er³⁺ doped CeO₂ shift to lower 2θ angle with increasing of Er³⁺ doping concentration, indicating that the unit length of the CeO₂ lattice was elongated. This system is supposed to strictly obey the Vegard's law and this peak shift should be proportional to the number of Ce⁴⁺ ions substituted for Er³⁺ ions. Hence, the lattice expansion is attributable to the substitution of dopant Er³⁺ ion (0.89 Å)[13] with ionic radius that is larger than that of Ce⁴⁺ ion (0.87 Å)[14].

Fig. 2 shows a conventional CeO₂ unit cell and a possible site variation of Er³⁺ doping in the CeO₂ crystal. CeO₂ has a fluorite structure (face-centered cubic unit cell with *Fm3m* space group) and Ce⁴⁺ is surrounded by eight O²⁻ ions. When trivalent

cations are doped in CeO₂, two Ce⁴⁺ ions are substituted by the dopants and an O²⁻ ion is removed to conserve the charge[15, 16]. In this figure, one oxygen vacancy is introduced for two Er³⁺ ions with the substitution of Er³⁺ for Ce⁴⁺ site, as the requirement of charge neutrality and stoichiometry. These changes of the lattice structure can be caused by formation of some defects in the CeO₂ host. The possible defect reaction is incorporation of Er³⁺ impurities into the CeO₂ crystals, which can be described in Kröger–Vink notation:

where O_O^x and Ce_{Ce}^x are an O²⁻ and a Ce⁴⁺ ion on their respective lattice sites, $V_O^{\cdot\cdot}$ represents an oxygen vacancy at the O²⁻ lattice site, and Er'_{Ce} means a Er³⁺ ion occupying the lattice site of a Ce⁴⁺.

This result is in accord with XRD patterns analysis. With the increase of Er³⁺ doping concentration, the lattice expansion of CeO₂:Er³⁺ becomes more and more obvious.

Fig. 3 shows the PL emission of CeO₂:Er³⁺ (5 at.%) film in visible and NIR regions. In visible region, the luminescence should be attributed to the intra $4f-4f$ transitions of Er³⁺ incorporated in CeO₂ host[17]. Three typical emission bands of Er³⁺ can be observed, and the luminescence peaks centered at 547 nm and 678 nm possess higher intensity than that at 526 nm. The emission peaks centered at 526 nm, 547 nm and 678 nm are assigned to the transitions $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$, respectively. Among these emission bands, the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition located at 678 nm possess higher intensity and selected as an emission source for excitation measurements. The PLE spectrum of the film monitored with 678 nm emission shows a broad excitation band at around 340 nm. In NIR region, the luminescence consists with an obvious emission extending from 1450 nm to 1600 nm and a weak emission at around 970 nm. The emission peaks centered at 970 nm and 1526 nm are assigned to the transitions $^4I_{11/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$, respectively. And monitored with 1526 nm, the PLE spectrum also shows a broad excitation band at around 340 nm. It should be noticed that the PLE spectra of the luminescence in visible and NIR regions are almost same shape and position. The excitations are

coincident to that obtained emissions to same ground state of Er^{3+} . It indicates that these two excitation bands have the same origin which are from host lattice.

The PLE spectra show a broad excitation band at around 340 nm, which is attributed to the charge transfer (CT) from O^{2-} to Ce^{4+} [18, 19]. The possible energy transfer mechanism in $\text{CeO}_2:\text{Er}^{3+}$ films under 340 nm excitation is shown in Fig. 4. The mechanism involves cooperative energy transfer (CET), multi-phonon relaxation (MPR), cross relaxation (CR) and excited state absorption (ESA). Excitation of Er^{3+} occurs mainly via CET from CT ($\text{O}^{2-} \rightarrow \text{Ce}^{4+}$) of CeO_2 to the $^4\text{F}_{7/2}$ level of Er^{3+} when excited with 340 nm. Then, the activated electrons in this level would quickly relax non-radiatively to the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels by MPR, which are $19,010\text{ cm}^{-1}$, $18,280\text{ cm}^{-1}$ and $14,750\text{ cm}^{-1}$ above the ground level. Subsequently, they relax radiatively to the $^4\text{I}_{15/2}$ ground state, leading to the 526 nm, 547 nm and 678 nm emissions. The luminescence multi-correlation peaks are related to Stark sub-level of the corresponding multiplet. The lowest Stark sub-level of $^2\text{H}_{11/2}$, the two Stark sub-level of $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ are populated through an energy transfer process[20]. Meanwhile, the electrons can also relax non-radiatively to $^4\text{I}_{9/2}$ level and these electrons at $^4\text{I}_{9/2}$ level experience a fast non-radiative decay to the $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ levels. Then the electrons decay to the ground state with the NIR emission of 970 and 1526 nm, and the band profile of emissions is related to stark level systems. It should be noticed that the emission intensity of 970 nm for transition $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ is very weak. It is possible due to CR and ESA processes. The CR channels are found to be CR1 ($^4\text{I}_{11/2} + ^2\text{F}_{5/2} \rightarrow ^4\text{I}_{13/2} + ^2\text{F}_{7/2}$), which can enhance the population of the $^4\text{I}_{13/2}$ level at the expense of the $^4\text{I}_{11/2}$ level[16, 21, 22]. Additionally, the possible CR channels are also found to be CR2 ($^4\text{F}_{7/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2} + ^4\text{F}_{9/2}$), CR3 ($^4\text{I}_{11/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2} + ^4\text{F}_{7/2}$) and CR4 ($^4\text{S}_{3/2} + ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2} + ^4\text{I}_{13/2}$). In the meantime, the electrons at $^4\text{I}_{11/2}$ level also can relax to $^4\text{I}_{13/2}$ level by non-radiative MRP. Then, 678 nm emission via $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ would be produced by absorbing another photon from adjacent Er^{3+} ion.

Fig. 5 shows visible PL emission spectra of $\text{CeO}_2:\text{Er}^{3+}$ films with different concentrations excited by 340 nm. The dependence of 547 nm and 678 nm emission

on Er^{3+} doping concentration is shown in the inset of Fig. 5. The PL intensity of 547 nm and 678 nm emissions are both affected by the Er^{3+} doping concentration. It is observed that the intensity of Er^{3+} emissions both increase with the increasing concentration, until it reached a maximum value and then decreases when concentration continues to increase. This phenomenon should be attributed to the substitution of Er^{3+} for Ce^{4+} site. Owing to the increasingly vacancy defects with increasing Er^{3+} concentration, quenching centers would be enhanced in the films. Therefore, Er^{3+} - Er^{3+} energy transfer also occurs due to the excessive concentration of Er^{3+} ions and the energy is transferred to the defects of films at last. It is indicated that more Er^{3+} ions transfer energy to nearby quenching centers and the probability of non-radiative transition will increase. The intensity of emissions decreased as a result of concentration quenching effect[23].

However, it should be noticed that the strongest PL intensity of 547 nm and 678 nm are obtained at different Er^{3+} concentration. The 547 nm emission reaches a maximum with 1 at.% Er^{3+} doping concentration and that of 678 nm is 5 at.%. And the intensity ratio $I(^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2})/I(^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2})$ decreases monotonously with the increase of the Er^{3+} concentration (inset (b) of Fig. 5). This fact is explained by the CR processes described in Fig. 4. Generally, CR processes are inefficient with low Er^{3+} concentration. As Er^{3+} concentration increases, the CR processes become more efficient due to shorter distance between the ions. Accordingly, increasing the processes of CR2 ($^4\text{F}_{7/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2} + ^4\text{F}_{9/2}$) and CR4 ($^4\text{S}_{3/2} + ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2} + ^4\text{I}_{13/2}$) result in increased population of the $^4\text{F}_{9/2}$ level and decreased population of the $^4\text{S}_{3/2}$ level, which lead to the increase of 678 nm emission intensity and the decrease of 547 nm emission intensity. Hence, with increasing Er^{3+} concentration, the relative intensity ratio of $I_{547 \text{ nm}}/I_{678 \text{ nm}}$ has a continuous decrease.

Fig. 6 shows NIR PL emission spectra of $\text{CeO}_2:\text{Er}^{3+}$ films with different concentrations excited by 340 nm. The dependence of 1526 nm emission on Er^{3+} doping concentration is shown in the inset of Fig. 6. Similar to the visible emissions, the PL intensity of 1526 nm emissions are also affected by the Er^{3+} doping concentration. The intensity of 1526 nm emission first increases and reaches a

maximum (when the concentration of Er^{3+} doping is 5 at.%), then remarkably decreases due to the concentration quenching effect. Therefore, the variation trend of NIR emission is the same with that of visible emission. Meanwhile, a zoomed PL emission spectra ranged in wavelength from 900 nm to 1100 nm is shown in the inset of Fig. 6. As can be seen in the figure, the 970 nm emission also owns the same variation trend.

4. Conclusion

$\text{CeO}_2:\text{Er}^{3+}$ films were achieved by electron-beam evaporation technique. Typical visible and NIR emission peaks were successfully obtained from the films annealed in air. The XRD analysis revealed that the process of Ce^{4+} ions substituted for Er^{3+} ions gave rise to lattice expansion. Additionally, the luminescence intensity of Er^{3+} and the intensity ratio red/green emission peaks were strong affected by Er^{3+} doping concentration. With the increase of Er^{3+} concentration, the intensity of Er^{3+} emissions increase until reached a maximum value and then decrease. Meanwhile, the intensity ratio $I(^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2})/I(^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2})$ decreases monotonously.

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Fig. 1. (a) XRD patterns of $\text{CeO}_2\text{:Er}^{3+}$ films at various Er^{3+} doping concentration. (b) The enlarged XRD patterns near 28.5° .

Fig. 2 Schematic diagram of a conventional CeO_2 unit cell and a possible site variation of Er^{3+} doping in the CeO_2 crystal.

Fig. 3 (a) Visible normalized PLE spectrum ($\lambda_{\text{em}}=678$ nm) and PL spectrum ($\lambda_{\text{ex}}=340$ nm) of annealed $\text{CeO}_2:\text{Er}^{3+}$ (5 at.%) film; (b) NIR normalized PLE spectrum ($\lambda_{\text{em}}=1526$ nm) and PL spectrum ($\lambda_{\text{ex}}=340$ nm) of annealed $\text{CeO}_2:\text{Er}^{3+}$ (5 at.%) film.

Fig. 4 Schematic sketch of energy transfer mechanism in $\text{CeO}_2:\text{Er}^{3+}$ films under 340 nm excitation.

Fig. 5 Visible PL emission spectra of $\text{CeO}_2:\text{Er}^{3+}$ films with different concentrations excited by 340 nm. (Insets show (a) the dependence of 547 nm and 678 nm emissions on Er^{3+} doping concentration and (b) the dependence of the intensity ratio $I(^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2})/I(^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2})$ on Er^{3+} doping concentration.)

Fig. 6 NIR PL emission spectra of $\text{CeO}_2:\text{Er}^{3+}$ films with different concentrations excited by 340 nm. (Insets show (a) the dependence of 1526 nm emissions on Er^{3+} doping concentration and (b) a zoomed PL emission spectra ranged in wavelength from 900 nm to 1100 nm.)