Photoluminescence enhancement in Yb^{3+}:Er^{3+} co-doped eutectic Al_2O_3: SiO_2 thin films by 980nm excitation

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Abstract: Si nanocrystals (nc-Si) are addressed in the eutectic Al_2O_3:SiO_2 thin films co-doped with Er^{3+} and Yb^{3+} by the laser-induced crystallization (LIC). The thin films are originally synthesized on a silica-on-silicon (SOS) substrate by the microwave electron cyclotron resonance (MW-ECR) plasma source enhanced RF sputtering. Raman spectroscopy has revealed that the strong crystallization occurs with the emergence of the nc-Si in the eutectic Al_2O_3: SiO_2 layer during the liquid phase transformation. The dual wavelength energy transfer mechanism at 800nm and 980nm induced by 980nm excitation in nc-Si and Yb sensitized Er doped system has been proposed and demonstrated. A tenfold photoluminescence enhancement has been obtained from this mechanism.

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1. Introduction

Yb^{3+} sensitized Er^{3+} doped Si material has been well studied as one of the promising materials for optoelectronic devices application assigned to the Er^{3+} emission at 1.54 μm, which lies in the minimum loss window of optic al communication related to silica-based device. However, temperature quenching and de-excitation in bulk Si crystal become a main drawback used as a host of Er^{3+}. Recently, many studies have described that the temperature quenching can be reduced drastically by adopting porous Si or Si nanocrystals (*nc*-Si) embedded in Er-doped SiO_2. Excitation emission from nc-Si generally has a continuous, strong, broad absorption wavelength range (λ<1μm) and a quasi-resonant transfer energy from nc-Si to Er^{3+} which enable nc-Si work as a powerful sensitizer via the energy exchange with Er^{3+} in $^4I_{9/2}$ to $^4I_{15/2}$ energy level instead of 800nm luminescence emission [1, 2]. Simultaneously, some studies reported the laser-induced crystallization (LIC) process as a potential approach to modify the microstructure and improve the crystal degree for imparting desirable host structure. High-power laser modification could provide a partial ultra-high temperature and control thermal penetration in a well-defined profile with rapid processing [5].

In this paper, we present a study about the LIC process to Yb^{3+}:Er^{3+} doped eutectic Al_2O_3: SiO_2 thin films on a silica-on-silicon (SOS) substrate by using a high-power output CO_2 laser. Aluminum oxide has been selected as the precursor host because of its' high thermal conductivity and high solubility of erbium than Silicon [4]. The Raman spectroscopy is investigated for the laser-induced effect on the crystallizing process of eutectic Al_2O_3: SiO_2 layer and suggested that nc-Si is addressed into eutectic layer from Si substrate under proper laser power and irradiation time control. The stronger PL emission improvement rather than the thermal annealing (TA) pure Al_2O_3 host has been observed by 980nm excitation at room temperature. The dual wavelength energy transfer (800nm and 980nm) under 980nm excitation induced by both nc-Si and Yb^{3+} has been proposed and demonstrated. The enhanced PL achieved from this structure is massive potential to the Er doped Si-based device application.

2. Raman spectroscopy and the LIC mechanism

Yb^{3+}:Er^{3+} doped Al_2O_3 thin films (~700nm) are initially deposited on a SOS substrate by the microwave electron cyclotron resonance (MW-ECR) plasma source enhanced RF sputtering. The substrate is acquired by oxidizing a 300nm silica layer on a Si substrate. The experimental setup and the deposition process have been described in our previous work [6]. The experimental parameters are determined under an Yb^{3+}:Er^{3+} ratio of 5:1 with an erbium content of 0.45mol%, for the maximum intensity of PL spectrum at 1.54 μm. The LIC treatment is carried out in the collimation system using a continuous wave carbon dioxide infrared laser operating at 10.6 μm with a 10ms pulse width [7]. For comparison, the same samples are annealed at 900^0C in air.

Raman spectroscopy in Fig 1 indicates that the deposited and the 900^0C TA Al_2O_3 thin films are mainly composed of amorphous structure. The only one peak at 520cm^{-1} originates from the silicon substrate. With the increase of the laser irradiation from 10ms to 1000ms, the 151 cm^{-1} and 480 cm^{-1}, a-Si; 950cm^{-1}, c-Si; 300 cm^{-1}, p-Si and 520cm^{-1}, nc-Si all appear to increase [8]. Stronger Raman peak at 520cm^{-1} accounted for (1) the formation of the nc-Si

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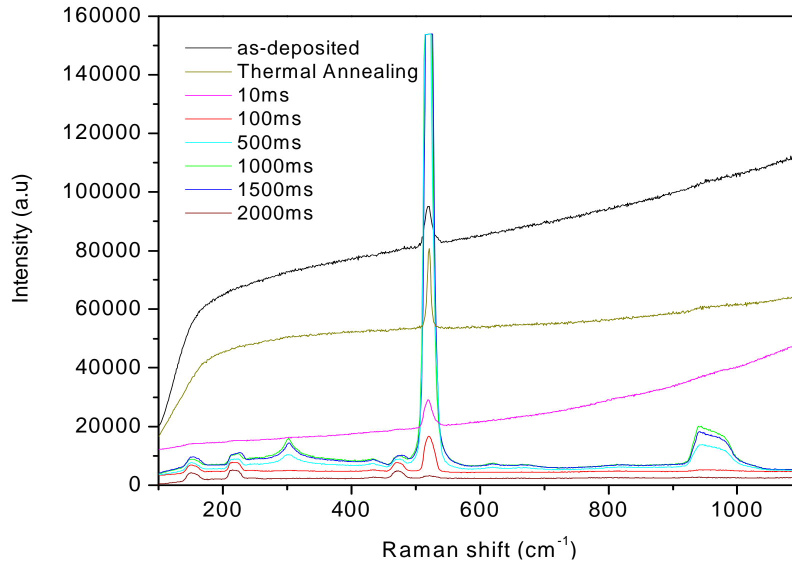

Fig. 1. Raman spectroscopy of Yb^{3+}:Er^{3+} co-doped Al_2O_3 thin films treated by laser-induced crystallization with different irradiation time. As reference the spectra for thermal annealing and as-deposited films are shown.

located at the boundary between the eutectic Al_2O_3:SiO_2 layer and the Si substrate and the diffusion of Si into Al_2O_3:SiO_2 environment [5]; (2) the development of the Al-Si-O structure in the SiO_2–Al_2O_3 melts, which is related to the 3-D network structure in vitreous SiO_2 and Al^{3+} substitution in it [9]. The peak position of 942 cm^{-1} band is broader and shifted to short-wavenumber position compared with that of the typical SiO_2 system, 950cm^{-1}. This shift indicates the combination of Al^{3+} and Si^{4+} in the aluminum silicate structures, because the frequency of the Al–O bond is lower than that of Si–O. The proposed crystallization mechanism is illustrated in Fig 2: when the crystallization threshold of the laser irradiation time is reached, the solid-phase crystallization process should occur in the Al_2O_3 thin films and more Al_2O_3 crystal is formed further instead of amorphous Al_2O_3 along with the direction of laser irradiation. The continuity of laser irradiation drives the crystallization depth to reach the Al_2O_3 layer, SiO_2 layer and Si substrate gradually, and the liquid-phase crystallization will replace the solid-phase crystallization in Al_2O_3 thin films. Then, the liquid crystallization process will dominate in the SiO_2 layer and Si substrate and urge them to melt and diffuse into Al_2O_3 layer.

The liquid-phase transformation leads to the Al_2O_3 layer and SiO_2 layer's melting into one eutectic Al_2O_3: SiO_2 layer. Because of the better heat conductibility between liquid-phase interface and solid-phase interface [10], strong crystallization occurs at the boundary between the liquid Al_2O_3: SiO_2 layer and Si substrate. All observed silicon crystallization results from the diffusion of Si from the substrate into the eutectic layer, the oxygen loss during the liquid-phase transformation and mainly the strong crystallization at the boundary. However, with the increase of irradiation time above 1000ms, the reversible process of silicon crystallization is also observed [11].

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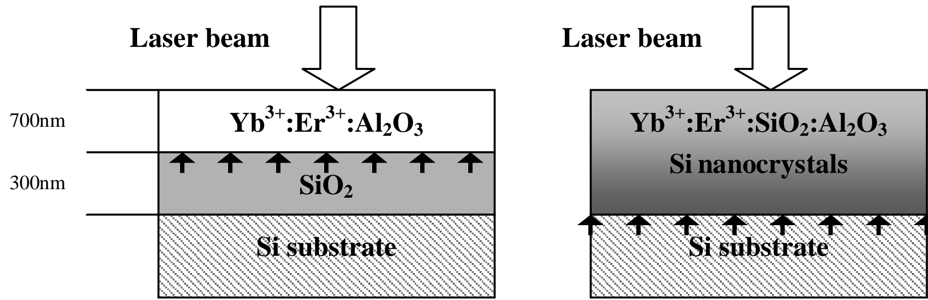

Fig. 2. Schematic representation of the laser-induced crystallization mechanism of Yb^{3+}:Er^{3+} co-doped eutectic SiO_2:Al_2O_3 thin films.

3. nc-Si sensitized 980nm excitation model and photoluminescence enhancement

Many reports have described that the presence of nc-Si in Er-doped SiO_2 enhances and expands the effective Er absorption cross-section when excited at 480nm. In this case, we choose 980nm as pump wavelength due to the more promising pump efficiency of Er ions and effective energy transfer between Yb ions and Er ions at this band [6]. In the eutectic Al_2O_3:SiO_2 layer, Al-Si-O structure can act as nested host and nc-Si and Er_2O_3 as lattice defects that are induced into host materials [9]. The excitation model described in fig 3 suggests: When nc-Si sensitized Yb:Er-doped system is pumped at 980nm, photons are absorbed by the nc-Si in which electrons are promoted from the valence band E_V to the conduction band E_{C1}, and are also absorbed by Yb ions and excite them to $^2F_{5/2}$. When an Er ion is addressed close to the nc-Si and Yb ions, the energy can be transferred from Ec_1 and $^2F_{5/2}$ to $^4I_{11/2}$ level of the Er ion. In the mean time, the population improvement in the $^4I_{11/2}$ strengthen the excite state absorption (ESA), cooperative upconversion (CUC) emission and back energy transfer (BET), which have been demonstrated to be the main restriction for the population inversion of $^4I_{13/2}$ in Yb:Er co-doped system in our previous work [6].

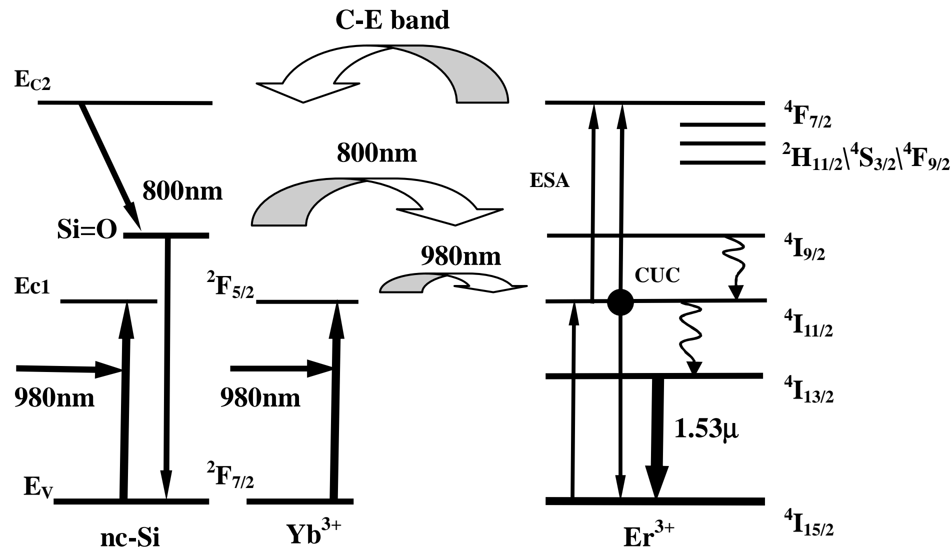

Fig. 3. The dual wavelength energy transfer diagram for nc-Si sensitized Yb:Er doped system excitation at 980nm.

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However, due to the existence of nc-Si, photons at CUC-ESA (C-E) emission band are absorbed by electrons in the nc-Si. Electrons in the E_V are promoted to E_{C2} and trapped by a Si=O interfacial state [9]. The recombination of the electron in this interfacial state with a hole in the E_V gives the light emission at 800nm [11]. Because of the magnificent absorption at C-E band and good couple between 800nm emission and the $^4I_{9/2}$ level of the Er, the strong C-E emissions of Er ions could been significantly reduced by nc-Si absorption and transferred to another pump wavelength corresponding to $^4I_{9/2}$ of Er ions. From $^4I_{9/2}$ level a rapid relaxation occurs to the $^4I_{11/2}$ level with a relaxation to the $^4I_{13/2}$ level and emission of photons at 1540nm. The Er ions are pumped by 800nm and 980nm wavelengths in the energy transfer interaction with nc-Si and Yb ions. This energy transfer mechanism could be described in fig 3 and by equation (1) and (2).

$$\frac{dN_{Si2}}{dt} = \sigma_{Si2} \cdot I_{C-E} \cdot N_{Si0} - \frac{N_{Si2}}{\tau_{Si}} - Ctr''' \cdot N_{Er0} \cdot N_{Si2} \qquad (1)$$

$$\frac{dN_{Yb1+Si1}}{dt} = I_P \cdot (\sigma_{Yb} \cdot N_{Yb0} + \sigma_{Si1} \cdot N_{Si0}) - \frac{N_{Yb1}}{\tau_{Yb}} - Ctr' \cdot N_{Er0} \cdot N_{Yb1} - Ctr'' \cdot N_{Er0} \cdot N_{Si1} \qquad (2)$$

Where σ_{Yb}, σ_{Si1}, σ_{Si2} are the light absorption cross-section of Yb ions at 980nm and nc-Si at 980nm and C-E band, respectively; I_P and I_{C-E} are the intensity of 980nm excitation photons and C-E emission photons. $I_{C-E}=\sum_{i}^{i=3} \hbar \nu_i n_i A_i$, here ν_i, n_i and A_i stands for the frequency, the population and the radiation transition probability according to $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$. N_{Er0}, N_{Yb0} and N_{Yb1} are the Er ions and Yb ions concentrations in the ground and the first excited states. N_{Si0}, N_{Si1}, N_{Si2} are the concentrations of Si nanocrystals corresponding to E_V, E_{C1} and E_{C2} exciton; *Ctr*', *Ctr*'' and *Ctr*''' are the coupling coefficients of the energy transfer from $^2F_{5/2}$ to $^4I_{11/2}$, from E_{V1} to $^4I_{11/2}$ and from CUC-ESA band to E_{C2}; τ_{Si} and τ_{Yb} are the radiation lifetimes of Si and Yb excitons.

Figure 4 shows the decay traces of luminescence emission at 800nm from nc-Si at room

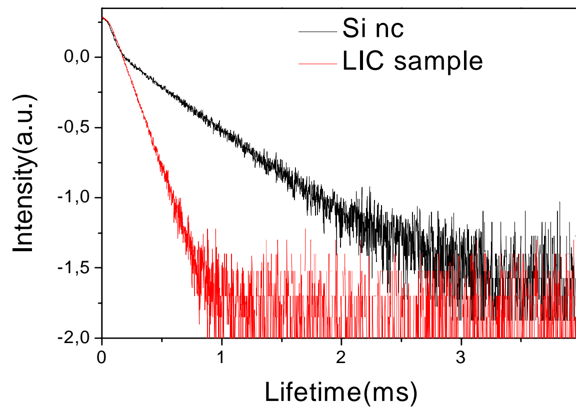

Fig. 4. The decay trace of 800nm luminescence emission of nc-Si sample and LIC sample.

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temperature. The only nc-Si sample and LIC sample are excited by a 457.9 nm line of an Ar-ion laser with a pulse width of 10ns and excited by 980nm semiconductor laser with a pulse width of 50ns respectively. The lifetime obtained from the sample not containing Yb and Er is about 0.41ms, while that from the sample with the Yb and Er concentration is about 0.22ms. The shortening of the PL lifetime of the nc-Si with the existence of Yb and Er ions implies that the energy transfer is arisen by photo-generated excitations, i.e., 800nm energy transfer to Er^{3+} is a preferential non-radiation recombination channel for nc-Si.

In order to demonstrate the non-radiation recombination from nc-Si to Er ions, we excite the LIC sample at 950nm waveband where Er has no absorption. For 950nm excitation, excitons are only absorbed by nc-Si and transferred to Er level $^4I_{11/2}$, instead of the direct absorption by Yb ions or Er ions. Fig 5 shows PL peak intensity corresponding to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition in Er^{3+} ions pumped at 980nm and 954nm, and the dependence of PL emission intensity and pump current. The PL intensity of TA sample and LIC sample reach saturation value under a pump current of 2000mA. At this point, PL peak intensity obtained from a laser irradiation with a laser fluence of 4J/cm^2, 1000ms is as 11.5 times high as that of TA sample at 900C^0. The PL intensity pumped by 950nm is much weaker than LIC sample and TA sample by 980nm excitation.

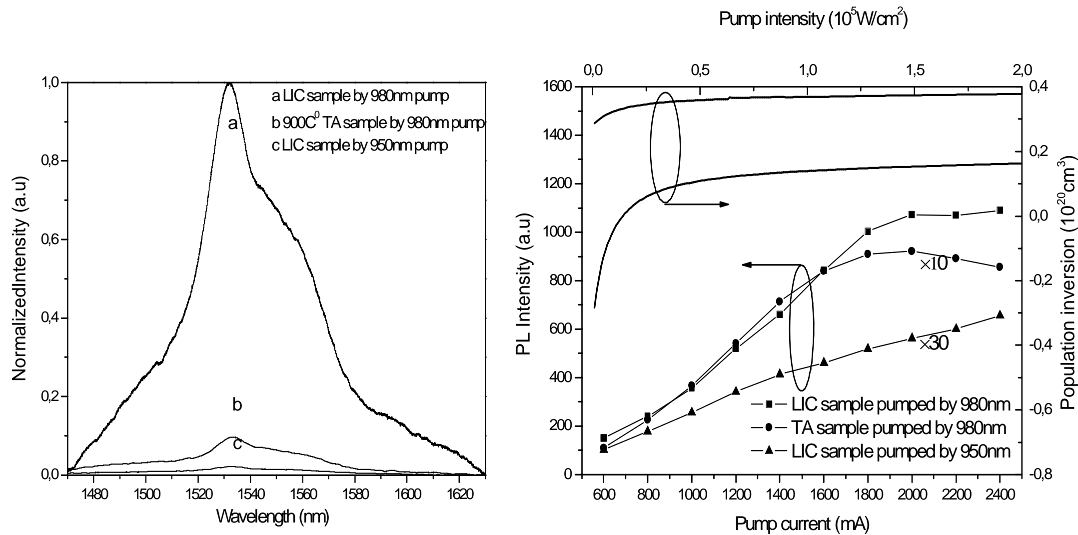

Fig. 5. (a) The PL intensity of LIC and TA samples pumped at 980nm and 950nm. Fig 5 (b) The PL intensity of LIC and TA samples as a function of pump current from 600mA to 2400mA. The simulation dependences of the population inversion between $^4I_{13/2}$ and $^4I_{15/2}$ in the nc-Si sensitized Yb:Er system and Yb:Er co-doped system and pump power are also shown in the different coordinate system.

We calculate the population inversion between $^4I_{13/2}$ and $^4I_{15/2}$ of Er^{3+} in SiO_2 containing nc-Si, Yb and Er ions, solving the rate equations (1) and (2). The parameters in calculation are obtained in Ref [2]. The Yb:Er doped system receive population inversion under a pump intensity of 1.45×10^4W/cm^2. In the nc-Si sensitized system, the population inversion is reached under a very low pump intensity (10W/cm^2), and the population inversion is improved by a factor of 3.5 at a nearly saturation pump intensity of 5×10^4W/cm^2. Qualitative numerical results display that the threshold of the population inversion of Er ions has been effectively reduced and the population inversion is achieved at low pump intensities due to the contribution of nc-Si.

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4. Conclusion

To summarize, we have grown the Yb^{3+}:Er^{3+} coped Al_2O_3 thin films on the SOS substrate by MW-ECR enhanced RF sputtering. The nc-Si is formed in the thin films by the pulsed CO_2 laser irradiation. Raman spectroscopy analysis suggests that the liquid-phase crystallization occurs in the LIC process, and the nc-Si in the eutectic Al_2O_3: SiO_2 crystal layer is formed depending on the irradiation time. The PL decay trace of nc-Si and the PL emission of Er^{3+} related to 950nm excitation are the direct evidences of the existence of resonant energy transfer processes between excitons in *nc*-Si and the second or the third excited states of Er^{3+}. The present results suggest that the emission of Er^{3+} ions sensitized by Yb^{3+} and nc-Si provides us a distinct tenfold improvement of PL intensity based on the dual wavelength energy transfer mechanism at 800nm and 980nm in nc-Si. This method is promising to obtain strong emission for rare-earth doped LED application, and a considerable optical gain with signal inducements, which could be applied to construct optical amplifiers in a high-level integrated configuration.

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