Processing and properties of ytterbium-erbium silicate thin film gain media

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The structural and photoluminescence properties of ytterbium-erbium silicate thin films have been investigated. The films were fabricated by RF-magnetron co-sputtering of Er₂O₃, Yb₂O₃, and SiO₂ on c-Si and subsequent annealing in N₂ or O₂ atmosphere.

I. INTRODUCTION

Erbium-doped materials have important applications in silicon photonics thanks to their strong light emission at 1535nm. This wavelength is particularly interesting, since it corresponds to the absorption minimum of silica optical fibers. However, the low solubility of erbium in silicon (around 10¹⁸cm⁻³) causes the photoluminescence (PL) to be too low to obtain gain with these materials. Recently, materials such as erbium oxide (Er₂O₃) and erbium silicates (Er₂SiO₅ and Er₂Si₂O₇), where erbium is a constituent rather than a dopant, have shown to be promising materials to solve this problem [1]-[3]. In these materials, the Er concentration can be made significantly higher (up to 10²²cm⁻³) than in Er-doped materials. However, it is expected that these materials with high Er concentration will suffer from upconversion at high pumping powers.

A novel strategy to reduce this upconversion is to work with ytterbium-erbium silicates, YbₓErₓSiO₅ and YbₓErₓSi₂O₇, where Yb³⁺ substitutes Er³⁺ in the silicate lattice and prevents neighboring Er³⁺ ions from causing upconversion. Additionally, as shown in Figure 1, the ⁷F₉/₂ → ⁴F₇/₂ transition in Yb³⁺ is resonant with the ⁴I₁₁/₂ → ⁴I₁₅/₂ transition in Er³⁺. Combined with the fact that the photon-absorption cross-section of Yb³⁺ at 980nm is about an order of magnitude higher than that for Er³⁺, this makes Yb³⁺ an excellent candidate to act as a sensitizer for the excitation of Er³⁺ [4].

In the present work, we have studied the structural and photoluminescence properties of ytterbium-erbium silicate thin films deposited on c-Si by means of RF-magnetron co-sputtering. The films were annealed for 1h in N₂ and O₂ atmospheres, at temperatures between 800°C and 1200°C. The presence of silicate phases after annealing at temperatures above 1000°C has been demonstrated with X-ray diffraction (XRD) analysis. Room-temperature PL experiments were carried out with 488nm and 980nm pumping light, causing direct excitation of the Er³⁺ and excitation through the Yb³⁺ ions respectively.

II. EXPERIMENTAL

The ytterbium-erbium silicate films were deposited by means of RF-magnetron co-sputtering of Er₂O₃, Yb₂O₃ and SiO₂ targets on crystalline p-type Si. The composition of the silicates was controlled by determination of the sputtering rate of each target as a function of applied power, and by varying the power applied to the different targets during co-sputtering accordingly. A deposition during 1h resulted in films of about 450nm thickness. The deposited films were annealed for 1h in N₂ and O₂ atmospheres in an annealing furnace. The annealing temperature was varied between 800°C and 1200°C in steps of 100°C.
X-ray diffraction experiments were carried out with a PANalytical X’Pert Pro diffractometer. The room-temperature photoluminescence experiments with 488nm pumping light were excited with an argon laser. The power was varied between 10mW and 100mW. The signal was detected with a liquid N\(_2\)-cooled photomultiplier tube. PL experiments with 980nm pumping light were done using a diode laser connected to an optical fiber which was vertically aligned above the sample. The emitted light was collected with another fiber aligned above the samples, connected to a spectrum analyzer.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

X-ray diffraction analysis was used to study the phase stability of the four component Yb-Er-Si-O system for different compositions and annealing conditions. The measurements show that the as-sputtered films are amorphous. For all compositions, the films remain amorphous after annealing at temperatures up to 900ºC in both N\(_2\) and O\(_2\). At higher temperatures, the XRD patterns for a particular composition and annealing temperature remain very similar for N\(_2\) or O\(_2\), which suggests that the annealing atmosphere for a furnace anneal does not affect the phase structure of the film.

The onset of crystallization typically occurs at 1000ºC or 1100ºC, depending on the ytterbium-erbium composition of the films. The peaks in the XRD patterns for films annealed at 1000ºC and 1100ºC correspond to a single monoclinic phase of Yb\(_2\)SiO\(_5\) or Er\(_2\)SiO\(_5\). Since both phases are indistinguishable, the XRD patterns are most likely due to a mixed Yb\(_{2-x}\)Er\(_x\)SiO\(_5\) phase. For the purpose of this project, a mixed phase is desired, since in this case the sensitization of Er\(^{3+}\) by Yb\(^{3+}\) and the reduction of upconversion will be better. The films annealed at 1200ºC again show peaks corresponding to a monoclinic phase of either Yb\(_2\)SiO\(_5\) or Er\(_2\)SiO\(_5\). Furthermore, peaks corresponding to a monoclinic phase of Yb\(_2\)Si\(_2\)O\(_7\) (disilicate) can be distinguished. The analysis clearly shows that silicates are the dominant stable phases after annealing at temperatures higher than 1000ºC.

B. Photoluminescence

Room temperature photoluminescence experiments under 488nm optical excitation were performed in order to investigate the silicate properties upon direct pumping of the erbium. It should be noted that Yb\(^{3+}\) does not have an energy level at this wavelength and consequently does not act as a sensitizer for Er\(^{3+}\) at this pumping wavelength. Figure 2 shows the PL spectrum around 1550nm of silicate films with a nominal composition of Yb\(_{1.8}\)Er\(_{0.2}\)SiO\(_5\) annealed for 1h in N\(_2\) at 1000ºC, 1100ºC and 1200ºC. The PL spectrum of a SRN:Er sample is shown as a reference. The latter spectrum is offset and scaled for clarity. Several features of the spectra in the figure attract attention. First of all, the figure shows that for the films annealed at 1000ºC and 1100ºC, the shape of the PL spectrum is similar to the spectrum of the SRN:Er sample. The main peak is only slightly shifted towards lower wavelengths (1532nm compared to 1534nm for the SRN:Er sample), whereas the secondary peak shifts from 1550nm for the SRN:Er sample to 1560nm for the silicate. This resemblance shows that the presence of Yb\(^{3+}\) does not alter the Er\(^{3+}\) emission around 1535nm. Secondly, it is seen that sharp peaks develop in the PL spectrum for the silicate film annealed at 1200ºC. The difference between the spectrum at 1000ºC (onset of crystallization) and the spectrum at 1200ºC demonstrates the transition from an amorphous matrix surrounding the Er\(^{3+}\) ions into a crystalline structure.

![Figure 2](image)

**Fig. 2.** Comparison of room temperature photoluminescence intensities around 1550nm of silicate films with nominal composition of Yb\(_{1.8}\)Er\(_{0.2}\)SiO\(_5\) annealed for 1h in N\(_2\) at 1000ºC, 1100ºC and 1200ºC. The PL spectrum of a SRN:Er sample is shown as a reference. The latter spectrum is offset and scaled for clarity. The PL was excited with 488nm laser light at a pump power of 20mW.

Figure 3 shows the integrated PL intensity of the Er emission at 1535nm and the PL lifetime for the silicate composition discussed in Figure 2, as a function of annealing temperature. All samples were annealed for 1h in N\(_2\), but the results for the films annealed in O\(_2\) were similar both in terms of magnitude and trends. The figure shows that the PL lifetime increases monotonically from 500\(\mu\)s to 2.1ms with increasing annealing temperature. Above that, it is seen that the integrated PL intensity and the lifetime follow approximately the same trend. This suggests that the increase in integrated PL intensity of this material is due to a reduction of the non-
radiative deexcitation mechanisms as crystallization takes place in the material.

Fig. 3. Room temperature integrated PL intensity and PL lifetime around 1535nm as a function of annealing temperature for a silicate film with nominal composition of Yb$_{1.8}$Er$_{0.2}$SiO$_5$. The film was annealed during 1h in N$_2$. The PL was excited with a 488nm laser at a pump power of 20mW.

Photoluminescence measurements with 980nm optical pumping were used to investigate the resonant energy transfer from Yb$^{3+}$ to Er$^{3+}$ and its effects on upconversion. Upon 980nm pumping, two mechanisms can cause excitation of the erbium: direct excitation of the erbium to the $^4$I$_{11/2}$ level, or excitation of the Yb$^{3+}$ into its $^2$F$_{5/2}$ level and subsequent energy transfer from Yb$^{3+}$ to Er$^{3+}$.

Figure 4 shows the upconversion measured for a silicate film with a nominal composition of Yb$_{1.8}$Er$_{0.2}$SiO$_5$, annealed in O$_2$ at 1100°C for 1h. It is seen that significant upconversion exists for 980nm pumping. The peaks clearly correspond to the different energy levels of erbium as shown in Figure 1. The peak at 490nm is expected to be a harmonic of the 980nm pumping laser and is not attributed to upconversion. The role of Yb$^{3+}$ in the upconversion process and the dependence on composition and annealing conditions is currently being studied.

IV. CONCLUSION

Yb$_{2-x}$Er$_x$SiO$_5$ films have been synthesized by means of RF-magnetron sputtering of Er$_2$O$_3$, Yb$_2$O$_3$ and SiO$_2$ on c-Si and subsequent annealing for 1h in N$_2$ or O$_2$ atmosphere. XRD measurements show the onset of crystallization at annealing temperatures between 1000°C and 1100°C. The crystalline phases formed are clearly identified as silicates, indicating that these are the dominant stable phases for high annealing temperatures. Room temperature PL measurements pumped with 488nm laser light show that the PL lifetime and integrated intensity for a nominal composition of Yb$_{1.8}$Er$_{0.2}$SiO$_5$ follow the same trend, indicating a reduction of non-radiative excitation mechanisms with increasing annealing temperature. The measured lifetimes increased from 0.5ms at 800°C to 2.1ms at 1200°C. PL measurements with 980nm pumping show clear erbium upconversion. The role of Yb$^{3+}$ in the upconversion mechanism and its relation to composition and annealing conditions need to be studied in detail.

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