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A comparison of silicon oxide and nitride as host matrices on the photoluminescence from Er^{3+} ions*

Ding Wu-Chang(丁武昌)†, Liu Yan(刘 艳), Zhang Yun(张 云),
Guo Jian-Chuan(郭剑川), Zuo Yu-Hua(左玉华), Cheng Bu-Wen(成步文),
Yu Jin-Zhong(余金中), and Wang Qi-Ming(王启明)

State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, *China*

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This paper compares the properties of silicon oxide and nitride as host matrices for Er ions. Erbium-doped silicon nitride films were deposited by a plasma-enhanced chemical-vapour deposition system. After deposition, the films were implanted with Er^{3+} at different doses. Er-doped thermal grown silicon oxide films were prepared at the same time as references. Photoluminescence features of Er^{3+} were inspected systematically. It is found that silicon nitride films are suitable for high concentration doping and the thermal quenching effect is not severe. However, a very high annealing temperature up to 1200 °C is needed to optically activate Er^{3+}, which may be the main obstacle to impede the application of Er-doped silicon nitride.

Keywords: Er doping, silicon nitride, photoluminescence
PACC: 7630K, 7855

1. Introduction

Er-doped silicon-based materials have been considered to be one of the most promising candidates to realize efficient silicon-based light emitters which are critical devices for optoelectronic applications. Since 1990s, Er-doped silicon has attracted considerable attention as it is completely compatible with CMOS processes. However, the energy back-transfer from Er^{3+} to silicon matrix and Auger recombination lead to inefficient Er^{3+} luminescence.[1−4] In 2000, Pavesi et al found optical gain in silicon nanocrystals embedded silicon dioxide matrix,[5] which activated widely research in this field. And it is proved that silicon nanocrystals can significantly enhance the efficiency of Er^{3+} luminescence.[6−8] Furthermore, light emitting devices with high efficiency based on Er-doped silicon oxide or silicon-rich-oxide materials have been fabricated,[9,10] which demonstrate that the silicon oxide is an appropriate host matrix for Er ions. Unfortunately, electron injection is difficult in these devices due to the wide band gap of silicon oxide and consequently very high biases are needed, which make the devices unstable. Therefore, in recent years, silicon nitride with a much smaller band gap has been extensively explored and efficient photoluminescence (PL) has been reported in both visible and infrared region in Er-doped silicon nitride (SiN_x).[11−14]

So, it is necessary to compare the properties of silicon oxide and nitride as host matrices for Er ions. In this paper, we have systematically inspected the PL features of Er^{3+} in silicon oxide and nitride films, including annealing temperature dependence, temperature quenching and concentration quenching effects. It was found that silicon nitride is appropriate for high concentration implantation while very high annealing temperature may be the main problem to impede Er-doped silicon nitride to be used in silicon photonics.

2. Experiment

Silicon nitride films were deposited on (100) silicon substrates by plasma-enhanced chemical-vapour deposition (PECVD) technique in a capacitively coupled reactor with a constant deposition pressure of 16 Pa. He-diluted 5% SiH_4 and NH_3 were used as precursor gases. The flow rates were 20sccm for SiH_4 and 40sccm for NH_3, respectively. The substrate temper-

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†E-mail: wcd04@semi.ac.cn

ature and the radio frequency (RF) power were kept constant at 300 °C and 50 W. The energy gap of the films is estimated to be 5.3eV due to linear optical absorption measurements. After deposition, the films were implanted with Er^{3+}at energy of 100 keV. Silicon oxide films were prepared by thermal oxidation at 1000 °C, which were implanted simultaneously with the silicon nitride films. All the films were estimated to be 100 nm thick by ellipsometer. Details of the samples are listed in Table 1. Though the peak concentration of Er is different for silicon oxide and nitride films at the same implantation dose, the equivalent Er amount assures the comparison to be sensible.

Table 1. Details of the samples involved. E_{Er} and D_{Er} are the implantation energy and dose, respectively. C_{Er} is the peak concentration of Er simulated by Trim 98.

label	host matrix	E_{Er}/keV	D_{Er}/(ions·cm^{-2})	C_{Er}/cm^{-3}
Ntr1	SiN_x	100	5×10^{13}	1.5×10^{19}
Ntr2	SiN_x	100	2×10^{14}	6×10^{19}
Ntr3	SiN_x	100	1×10^{15}	3×10^{20}
Ox1	SiO_2	100	5×10^{13}	2×10^{19}
Ox2	SiO_2	100	2×10^{14}	8×10^{19}
Ox3	SiO_2	100	1×10^{15}	4×10^{20}

After implantation, the samples are cleaved into pieces and annealed at different temperatures for one hour under N_2 ambient. The PL spectra measurements were carried out by using an HR 800 Micro-Raman spectrometer, and a 488 nm Ar^+ laser was employed as the excitation light source. The excitation power was fixed at about 30 mW. A silicon CCD was used for visible PL detection and a liquid nitrogen cooled InGaAs detector was employed for the infrared PL inspection.

3. Results and discussion

Figure 1(a) shows the classical PL of Ntr3 in visible range at room temperature after 1200 °C annealing. The PL spectra can be analytically decomposed into two curves: a broad Gaussian band located at about 700 nm and a several-peaks spectrum ascribed to Er^{3+} luminescence. The Gaussian band is most likely due to Er-implantation induced defects or the formation of silicon nanoclusters.[15] However, the luminescence from Er^{3+} is quite complicated. The strongest peaks are located at around 524 nm, 550 nm and 853 nm, which are labeled in Fig.1. These resolved PL peaks are due to the transitions from the energy levels $^2H_{11/2}$ and $^4S_{3/2}$ to the ground state (524 nm, 550 nm) or the first excited state (853 nm),[16–20] which are denoted in Fig.2. Due to the fact that $^2H_{11/2}$ and $^4S_{3/2}$ are the closest energy levels to $^4F_{7/2}$ which can resonantly absorb the 488 nm excitation light, the Er^{3+} is most likely excited by direct pumping. The Er^{3+} is firstly pumped to $^4F_{7/2}$ energy level, then quickly decays to $^2H_{11/2}$ and $^4S_{3/2}$, and radiative recombinations from these two levels result in

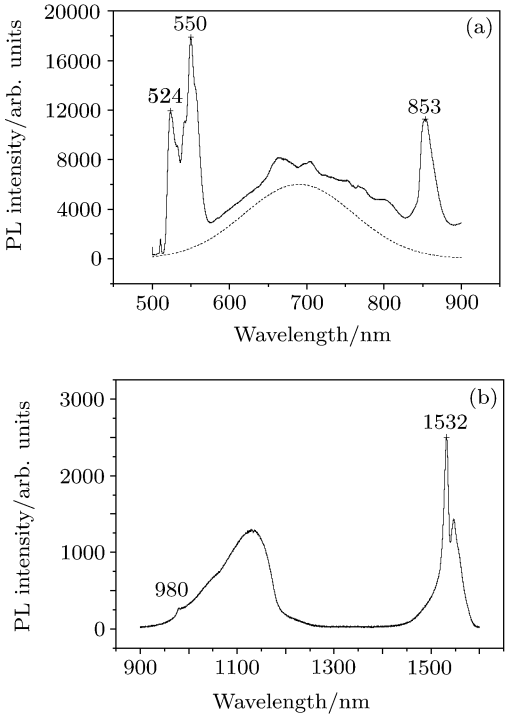


Fig.1. Visible PL (a) and infrared PL (b) of Er-doped silicon nitride films (Ntr3) at room temperature after 1200 °C annealing. The dot line is a Gaussian peak which is independent of Er^{3+} luminescence. The broad band around 1130nm is from silicon substrate.

strong PL. For Er-doped silicon oxide, the properties of the visible PL (not shown) are similar except that the peaks have more details. Based on this fact, the PL from these two materials are comparable as the excitation mechanisms are the same. Infrared PL spectrum of Ntr3 is illustrated in Fig.1(b) with strong 1532 nm Er^{3+} luminescence. The 980 nm luminescence of Er^{3+} can also be seen in Fig.1(b), which is superimposed on a broad band emission of silicon substrate.

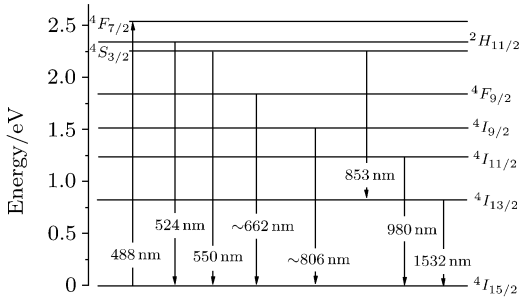


Fig.2. Energy-level diagram of Er^{3+} ions. Transitions and corresponding PL peaks are denoted in the figure.

Figure 3 shows the integrated PL intensity of Ox3 and Ntr3 after different annealing temperatures. The integrating range is from 1400 nm to 1600 nm, for the 1540 nm peak is most concerned in silicon photonics application. For Ox3, the optimum annealing temperature is about 800 °C and the PL intensity sharply declines for higher annealing temperature. It is well known that the annealing process removes implantation defects like dangling bonds and vacancy complexes, and results in enhancement of the PL intensity. But Er precipitation leads to the sudden drop after annealing above 800 °C.[19] However, for Ntr3, the PL arises only when the annealing temperature is higher than 900 °C, and the PL intensity has an positive correlation with the annealing temperature. An optimum annealing temperature should be 1200 °C or higher, which cannot be decided due to the temperature limitation of our tube furnace. Such a high temperature is not compatible with CMOS processes, which may impede the application of the Er-doped silicon nitride films. In fact, strong PL has been observed in as-implanted Ox3 films, as Polman has demonstrated that annealing treatment is not necessary to obtain optically active Er^{3+}.[19] However, for Ntr3, the annealing treatment is essential to optically activate Er^{3+}, for the electronegativity of N is smaller than O. Therefore high temperature is a must for Er and N atoms to form a chemical bond.

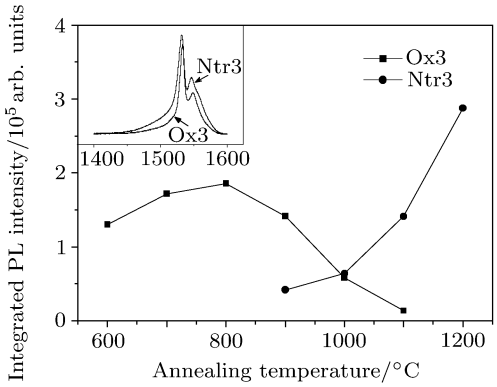


Fig.3. Integrated PL intensity of Ox3 and Ntr3 after different annealing temperature. The inset picture is an example of Er^{3+} PL.

At the optimum annealing conditions of the two samples, i.e. 800 °C for Ox3 and 1200 °C for Ntr3, the PL spectra are shown in the inset of Fig.3. The main differences should be the spectrum widths which are 9.7 nm and 14.1 nm for Ox3 and Ntr3, respectively. Er-doped silicon nitride has a much wider range photoluminescence due to the asymmetrical environment in silicon nitride films. The transition from $^4H_{13/2}$ to $^4H_{15/2}$ is forbidden by selection rules. So the asymmetrical crystal field disturbance can partially break the law and lead to PL intensification. In fact, the integrated PL intensity is enhanced by a factor around 1.5 for Er-doped silion nitride in comparison with Er-doped silicon oxide.

Temperature quenching effects of Ntr3 and Ox3 are illustrated in Fig.4. The annealing temperature is 800 °C for Ox3 and 1200 °C for Ntr3. As the rise of measured temperature, the integrated PL intensity is slowly depressed for both Er-doped silicon oxide and nitride films. From 80 K to 273 K, the intensity decreased 14.4% and 14.9%, respectively. The insignificant temperature quenching effect is ascribed to the

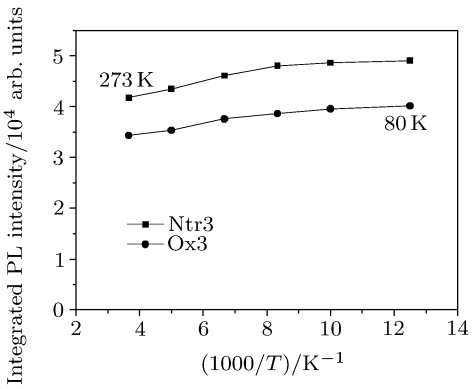


Fig.4. Temperature evolution of PL from Er-doped silicon oxide and nitride films.

large band gap of the two matrices which suppresses the energy back transfer and Auger processes.[1,2] Also the results indicate that the PECVD grown silicon nitride films have low density of thermal-activated non-radiative defects after annealing at high temperature, for the temperature evolution of Er^{3+} PL is similar in comparison with Er-doped silicon dioxide.

Another concerned phenomenon in Er-doped materials is concentration regression of the PL intensity.[21,22] For the samples mentioned in this paper, such an effect has not been observed. The integrated PL intensity intensifies along with the enhancement of Er concentration. However, the utilization ratio of Er atoms declines as the Er concentration increases for both silicon oxide and nitride films. For this inspection, the integrated PL intensity divided by Er-implantation dose is defined as the indicator of Er utilization ratio. Figure 5 shows the variation of Er utilization ratio versus Er-implantation dose. At low implantation dose, the Er utilization ratio in silicon oxide is higher than that in silicon nitride. However, the concentration enhancement leads to dramatic drop of the Er utilization ratio in silicon oxide. When the implantation dose is 1×10^{15} cm^{-2}, the Er utilization ratio of Er-doped silicon nitride surpasses Er-doped silicon oxide. Though the utilization ratio is degraded for both host matrices, it is suggested that the silicon nitride is a better host matrix for very high concentration Er-implantation.

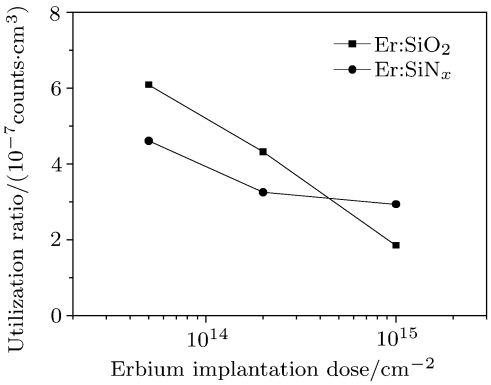


Fig.5. The variation of Er utilization ratio versus Er implantation dose. The annealing temperatures for Er-doped silicon oxide and nitride films are 800 °C and 1200 °C, respectively.

4. Conclusion

In conclusion, Er^{3+} photoluminescence from Er-doped silicon nitride and oxide films were inspected systematically. Compared to Er-doped silicon oxide, Er-doped silicon nitride films have following features: (1) A very high annealing temperature is needed to activate Er^{3+}, as the N atom has a low electronegativity and it is hard for Er bonding to N. Also high temperature annealing can remove the implantation defects leading to strong luminescence of Er^{3+}. (2) No significant temperature quenching effects have been observed. The silicon nitride film has a large band gap and low density of thermal-activated non-radiative defects. (3) The Er utilization ratio declines as the Er-concentration increasing. However, the silicon nitride film is more suitable for very high concentration doping.

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