

Photoluminescence spectroscopy of sputtering Er-doped silicon-rich silicon nitride films*

Ding Wuchang(丁武昌)^{1,†}, Zuo Yuhua(左玉华)¹, Zhang Yun(张云)¹, Guo Jianchuan(郭剑川)¹,
Cheng Buwen(成步文)¹, Yu Jinzhong(余金中)¹, Wang Qiming(王启明)¹,
Guo Hengqun(郭亨群)², Lü Peng(吕蓬)², and Shen Jiwei(申继伟)²

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

(2 College of Information Science and Engineering, Huaqiao University, Quanzhou 362021, China)

Abstract: Er-doped silicon-rich silicon nitride (SRN) films were deposited on silicon substrate by an RF magnetron reaction sputtering system. After high temperature annealing, the films show intense photoluminescence in both the visible and infrared regions. Besides broad-band luminescence centered at 780 nm which originates from silicon nanocrystals, resolved peaks due to transitions from all high energy levels up to ${}^2H_{11/2}$ to the ground state of Er^{3+} are observed. Raman spectra and HRTEM measurements have been performed to investigate the structure of the films, and possible excitation processes are discussed.

Key words: photoluminescence; silicon nitride; Er doping

DOI: 10.1088/1674-4926/30/10/102001

PACC: 7855; 7630K

1. Introduction

Since the pioneering work of Canham *et al.* in the 1990s^[1], several scientific and technological breakthroughs have opened new exciting routes to turn Si into an efficient light emission material. In particular, Er-doped silicon-based materials have attracted considerable interest due to their promising future in the development of light-emitting diodes and lasers operating at a wavelength of 1.54 μm , which coincides with the absorption minimum of silica optical fibers. Among these materials, Er-doped silicon-rich silicon oxide (SRO) is considered to be the most promising for photonics application. Strong silicon nanocrystal (NC-Si) mediated Er^{3+} luminescence has been proved in SRO films^[2-4], which leads to enhancement of the luminescence efficiency of Er^{3+} . Light-emitting devices with high efficiency based on Er-doped SRO materials have also been fabricated^[5,6]. However, in these devices, electron injection is difficult due to the wide band gap of the silicon oxide matrix 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 the visible and infrared regions in Er-doped SRN films^[7-9]. Despite these achievements, the mechanism of the PL is still unclear and under discussion.

The present contribution reports strong PL in both the visible and infrared regions from sputtering Er-doped SRN films. After high temperature annealing, all radiative transitions of Er^{3+} with wavelengths longer than 500 nm have been

observed.

2. Experiment

Er-doped SRN films of 1.5 μm thickness were deposited on (100) silicon wafers by an RF magnetron reaction sputtering system. A silicon disc (99.999% purity, 8.0 cm in diameter) partially covered by several small Er platelets on the surface was used as the target and nitrogen was used as the reactant gas. The area ratio of Er platelets was about 1% and the gas flow rates of argon and nitrogen were 100 sccm and 10 sccm, respectively. The temperature of the substrates and the RF power were kept constant at 300 °C and 300 W. After deposition, the samples were then cut into pieces and annealed at different temperatures under N_2 ambient for 1 h. The same films were also deposited on quartz substrates for Raman scattering inspection. Raman and visible photoluminescence spectra measurements were carried out 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 5 mW. Infrared photoluminescence was measured using another micro-spectra system equipped with a liquid-nitrogen-cooled Ge detector and the excitation light source was a 514 nm Ar^+ laser. All these measurements were carried out at room temperature. The linear optical absorption property of the as-deposited films was measured with a Unico UV-2800H spectrometer, and therefore the optical band gap E_g of the samples is estimated to be 1.58 eV, indicating the films are silicon-rich. Rutherford backscattering spectrometry (RBS) inspection

* Project supported by the National Natural Science Foundation of China (No. 60336010) and the State Key Development Program for Basic Research of China (No. 2006CB302802).

† Corresponding author. Email: wcd04@semi.ac.cn

Received 5 March 2009, revised manuscript received 13 May 2009

© 2009 Chinese Institute of Electronics

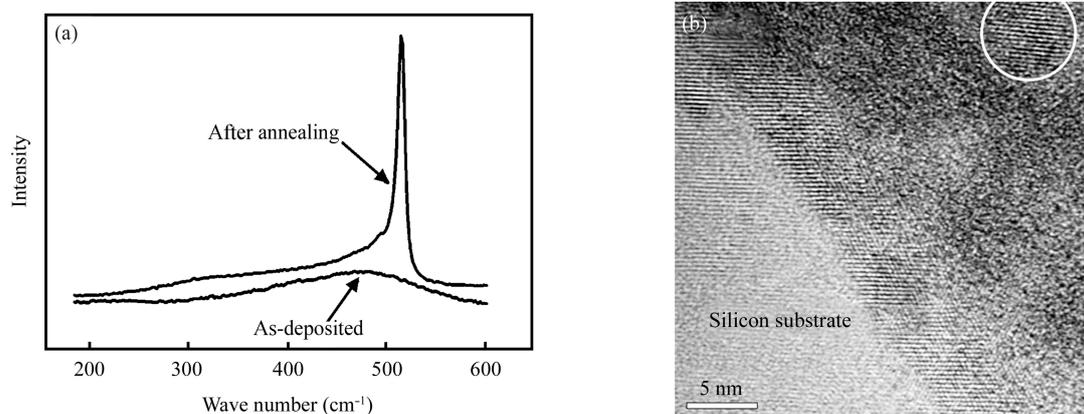


Fig. 1. (a) Raman spectra of samples before and after annealing at 1100 °C; (b) HRTEM image of 1100 °C annealed films. The circle illustrates a typical silicon nanocrystal.

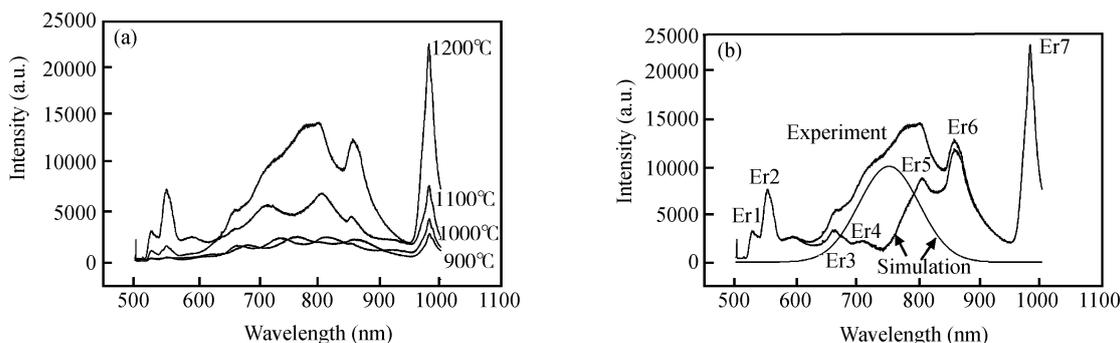


Fig. 2. (a) Visible PL from the Er-doped SRN films annealed at different temperatures for 1h; (b) An example of the decomposition of the PL spectra.

confirmed that the Si concentration is 55 at.% and the Er concentration is 3.5 at.%.

3. Results and analysis

Figure 1(a) shows the Raman spectra of the sputtering films. Before annealing, the Raman spectra show a broad peak at 474 nm which is due to amorphous silicon clusters^[10], indicating that the SRN films already contain small silicon nanostructures even without high temperature annealing. After 1100 °C annealing, the sharp 516 cm⁻¹ peak of the transverse optical mode of crystalline silicon arises due to phase separation of silicon and silicon nitride, and crystallization of the silicon nanoclusters. HRTEM measurements confirmed the existence of silicon nanocrystals after the annealing process. For samples annealed at 1100 °C, silicon nanocrystals with diameter of 5 nm can be obviously observed in the TEM image, which is shown in Fig. 1(b). However, only a few small silicon nanocrystals with diameters of about 1 nm can be seen after annealing at 1000 °C, and silicon nanocrystals are completely absent in the TEM images for samples annealed below 1000 °C.

Visible PL from the deposited films is prominent only when the annealing temperature is higher than 900 °C, and the PL intensity is enhanced as the annealing temperature is increased. Typical PL spectra, which are very complicated, are shown in Fig. 2(a). In order to find the origination of the PL,

the spectra were mainly decomposed into two curves: a broad Gaussian band located at about 780 nm which is supposed to be the contribution of NC-Si, and a resolved six-peak spectrum ascribed to Er³⁺ luminescence. Figure 2(b) is an example of the decomposition of the PL spectra. The peaks of Er³⁺ luminescence are marked with Er1–Er6, and are due to transitions of high energy levels to the ground state and the ⁴S_{3/2} → ⁴I_{13/2} transition of Er³⁺ ions. All these transitions and corresponding references are summarized in Table 1. The photoluminescence intensities from Er³⁺ and NC-Si are both sensitive to the annealing temperature. With rising annealing temperature, phase separation of silicon and silicon nitride matrix causes precipitation of NC-Si, resulting in enhancement of the broad band luminescence peak at 780 nm. Meanwhile, the bonding of erbium and nitrogen atoms at high temperature optically activates the Er³⁺ ions and consequently causes the improvement of Er³⁺ PL. However, since the PL intensities of NC-Si and Er³⁺ are both proportional to the annealing temperature, no optimum temperature was found due to the limitation of our furnace.

Another characteristic of the PL spectra is an oscillation feature ranging from 650 to 900 nm, especially when the annealing temperature is below 1000 °C. For higher annealing temperatures such as 1200 °C, after Gaussian band subtraction, the oscillation feature can also be observed. According to Negro^[9,11], the PL from NC-Si embedded silicon nitride films has a complicated shape with several peaks, which may be due

Table 1. Transitions responsible for the Er³⁺ luminescence peaks.

Peak label	Peak position	Transition responsible for the peak	Reference
Er1	525 nm	$^2H_{11/2} \rightarrow ^4I_{15/2}$	Refs.[12, 13]
Er2	550 nm	$^4S_{3/2} \rightarrow ^4I_{15/2}$	Refs.[12, 13]
Er3	~ 660 nm	$^4F_{9/2} \rightarrow ^4I_{15/2}$	Refs.[12, 13]
Er4	~ 800 nm	$^4I_{9/2} \rightarrow ^4I_{15/2}$	Refs.[14, 15]
Er5	855 nm	$^4S_{3/2} \rightarrow ^4I_{13/2}$	Refs.[14, 15]
Er6	980 nm	$^4I_{11/2} \rightarrow ^4I_{15/2}$	Refs.[13, 14, 15]

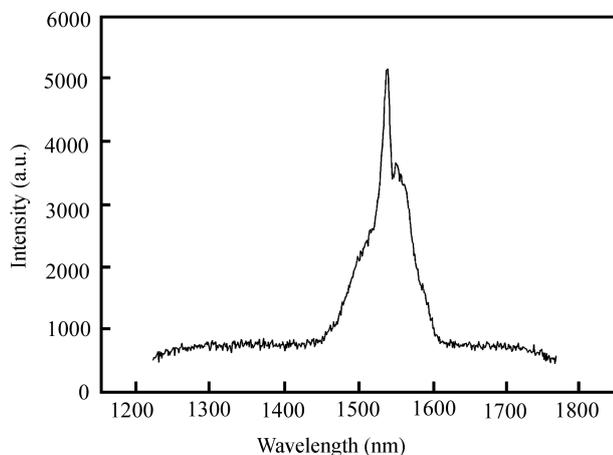
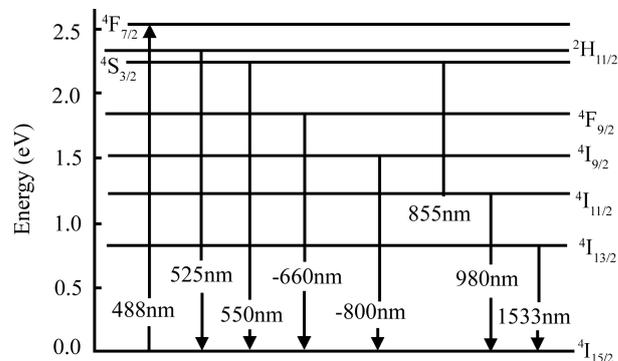


Fig. 3. Infrared PL spectrum from Er-doped SRN films annealed at 1100 °C for 1 h.

to the combination of the luminescence from NC-Si and the surface states. These multiple mechanisms could be responsible for the complicated PL features in our case. However, as the Er ion luminescence begins, it is hard to clarify the mechanisms. In general, it is suggested that the PL from Er-doped SRN films could be a combination of NC-Si luminescence modified by surface states and Er³⁺ ion luminescence.

A strong infrared PL spectrum from the annealed Er-doped SRN films has been obtained, and is shown in Fig. 3. The peak position is around 1.54 μm, which is well known as the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ ions. The peak at 1.55 μm is due to crystalline field splitting of the ground state $^4I_{15/2}$ of Er³⁺ ions. Infrared PL is again prominent only when the annealing temperature is higher than 900 °C, indicating that bonding of Er and N atoms is critical for the activation of Er³⁺.

However, the excitation mechanism is still unclear. Usually, NC-Si is an efficient sensitizer of Er³⁺ luminescence^[3]. Since the energy levels of $^2H_{11/2}$ and $^4S_{3/2}$ of Er³⁺ ions can not be activated by energy transfer from NC-Si, it is more likely that the Er³⁺ ions are stimulated from direct absorption of the excitation source. Though the up conversion concept has generally been recognized in Er-doped materials^[16, 17], the up conversion process is inefficient compared to direct excitation of the pump laser. Figure 4 shows a schematic illustration of the excitation and transitions of Er³⁺; the corresponding PL peaks are denoted in the figure while the energy splitting due to the crystalline field of the SiN_x matrix is not mentioned. Another excitation routine is through absorption by the SiN_x matrix and

Fig. 4. Energy-level diagram of Er³⁺ ions. Transitions and corresponding PL peaks are denoted in the figure.

energy transfer from SiN_x to Er³⁺^[19], which is possible for the present work. The energy transfer between NC-Si and Er³⁺ is also obscure. More evidence is required to verify these mechanisms.

4. Conclusion

In conclusion, Er-doped SRN films were prepared by the RF magnetron reaction sputtering technique. After high temperature annealing, resolved photoluminescence of Er³⁺ ranging from 500 nm to 1.6 μm was observed, due to transitions between different energy levels of Er³⁺. Also, broad band photoluminescence originating from NC-Si has been proved. HRTEM and Raman measurements were performed to verify the structure of the films and the formation of NC-Si has been confirmed. It is suggested that the strong PL from Er-doped SRN films is a combination of NC-Si luminescence modified by surface states and Er³⁺ ion luminescence.

Acknowledgements

The authors are indebted to Yang H T and Zhang L N *et al.* at Tsinghua-Foxconn Nanotechnology Research Center for Raman and TEM measurements. The authors also acknowledge Professor Zhu H L (ISCAS) for the infrared PL measurements.

References

- [1] Cullis A G, Canham L T. Visible light emission due to quantum size effects in highly porous crystalline silicon. *Nature*, 1991, 353: 335

- [2] Fujii M, Yoshida M, Kanzawa Y, et al. 1.54 μm photoluminescence of Er^{3+} doped into SiO_2 films containing Si nanocrystals: evidence for energy transfer from Si nanocrystals to Er^{3+} . *Appl Phys Lett*, 1997, 71: 1198
- [3] Pacifici D, Franzò G, Priolo F, et al. Modeling and perspectives of the Si nanocrystals–Er interaction for optical amplification. *Phys Rev B*, 2003, 67: 245301
- [4] Kik P G, Polman A. Exciton-erbium energy transfer in Si nanocrystal-doped SiO_2 . *Mater Sci Eng B*, 2001, 81: 3
- [5] Iacona F, Pacifici D, Irrera A, et al. Electroluminescence at 1.54 μm in Er-doped Si nanocluster-based devices. *Appl Phys Lett*, 2002, 81: 3242
- [6] Sun J M, Skorupa W, Dekorsy T, et al. On the mechanism of electroluminescence excitation in Er-doped SiO_2 containing silicon nanoclusters. *Opt Mater*, 2005, 27: 1050
- [7] Park N M, Choi C J, Seong T Y, et al. Quantum confinement in amorphous silicon quantum dots embedded in silicon nitride. *Phys Rev Lett*, 2001, 86: 1355
- [8] Bell M J V, Nunes L A O, Zanatta A R. Optical excitation of Er^{3+} ions in a-SiN alloys. *J Appl Phys*, 1999, 86: 338
- [9] Negro L D, Yi J H, Kimerling L C, et al. Light emission from silicon-rich nitride nanostructures. *Appl Phys Lett*, 2006, 88: 183103
- [10] Zi J, Büscher H, Falter C, et al. Raman shifts in Si nanocrystals. *Appl Phys Lett*, 1996, 69: 200
- [11] Negro L D, Yi J H, Michel J, et al. Light emission efficiency and dynamics in silicon-rich silicon nitride films. *Appl Phys Lett*, 2006, 88: 233109
- [12] Zanatta A R, Ribeiro T M, Jahn U. Visible luminescence from a-SiN films doped with Er and Sm. *Appl Phys Lett*, 2001, 79: 488
- [13] Hömmerich U, Seo J T, Abernathy C R, et al. Spectroscopic studies of the visible and infrared luminescence from Er doped GaN. *Mater Sci Eng B*, 2001, 81: 116
- [14] Hoven G N, Snoeks E, Polman A, et al. Upconversion in Er-implanted Al_2O_3 waveguides. *J Appl Phys*, 1996, 79: 1258
- [15] Polman A. Erbium implanted thin film photonic materials. *J Appl Phys*, 1997, 82: 1
- [16] Jaba N, Kanoun A, Mejri H, et al. Infrared to visible up-conversion study for erbium-doped zinc tellurite glasses. *J Phys: Condens Mater*, 2000, 12: 4523
- [17] Xiao S G, Yang X L, Liu Z W, et al. Up-conversion in $\text{Er}^{3+}:\text{Y}_2\text{O}_3$ nanocrystals pumped at 808 nm. *J Appl Phys*, 2004, 96: 1360
- [18] Negro L D, Yi J H, Michel J, et al. Light-emitting silicon nanocrystals and photonic structures in silicon nitride. *IEEE J Sel Top Quant*, 2006, 12: 1628