Eye-safe 2 μm luminescence from thulium-doped silicon

Manon Lourenço,* Russell Gwilliam, and Kevin Homewood

Advanced Technology Institute, Faculty of Engineering and Physical Sciences,
University of Surrey, Guildford, Surrey, GU2 7XH, UK

*Corresponding author: m.lourenco@surrey.ac.uk

Received October 27, 2010; revised December 6, 2010; accepted December 8, 2010;
posted December 9, 2010 (Doc. ID 137302); published January 10, 2011

We report on photoluminescence in the 1.7–2.1 μm range of silicon doped with thulium. This is achieved by the implantation of Tm into silicon that has been codoped with boron to reduce the thermal quenching. At least six strong lines can be distinguished at 80 K; at 300 K, the spectrum is dominated by the main emission at 2 μm . These emissions are attributed to the trivalent Tm^{3+} internal transitions between the first excited state and the ground state. © 2011 Optical Society of America

OCIS codes: 250.5230, 140.3070, 160.5690, 160.6000.

Light emission in the eye-safe 2 μm region is of considerable interest, in particular for medical applications, but also for gas sensing systems and direct free space optical communications. Although 2 μm Tm lasers are now commercially available [1], they are fabricated only in insulating crystals and fiber materials and as a result can be pumped only optically. To achieve electrical pumping, a semiconductor host is required. Because competing radiative transitions across the bandgap are detrimental, indirect rather than direct gap semiconductors are the preferred host, and of these, silicon is by far the most technologically important. In addition, loss mechanisms such as two-photon absorption are reduced by orders of magnitude in indirect rather than direct gap transitions because of the need for the involvement of phonons to conserve momentum.

The incorporation of rare-earth (RE) elements into semiconductors, crystals, and glass fibers has been extensively used as optical sources in such materials. The optical transitions that originate from the RE partially filled inner 4*f* shell are sharp and generally insensitive to the host and temperature variations and can enable light emission throughout the visible to the IR regions. Among the RE elements, thulium is a particularly interesting optical source. The transitions between the three Tm^{3+} lower excited states (3H_4 , 3H_5 , and 3F_4) and the ground state (3H_6) can lead to light emission in the 0.8, 1.2, and 2.0 μm regions [2]. Luminescence in the 1.2 μm range has been observed in silicon substrates incorporating Tm, and a Tm:Si-based LED operating at low forward bias has been demonstrated [3,4]. Light emission in the 0.8–2.0 μm range from III-V substrates doped with Tm has also been shown—a summary of previously published work can be found in [3]. A Tm:YAG laser operating at 2 μm was first demonstrated in 1965 [5] and has led to commercial lasers being fabricated in a variety of host crystals and fiber materials [1]. In this Letter, we report on photoluminescence (PL) in the 1.7–2.1 μm region from silicon substrates doped with Tm.

Samples were fabricated by ion implantation of 10^{13}Tm cm^{-2} at 400 keV into an *n*-type Si [100] substrate (2–7 $\Omega\text{ cm}$) previously implanted with 10^{15}B cm^{-2} at 30 KeV. Subsequently samples were annealed in a nitrogen atmosphere at 850 °C for 1, 5, and 15 min. As a reference, Tm was also implanted at the same dose and energy into a Si substrate that did not contain boron

and subsequently annealed at the same conditions as the boron codoped samples. PL measurements in the 80–300 K range were performed in the 1.0–2.3 μm region using a liquid-nitrogen-cooled InGaAs detector. Samples were mounted in a liquid-nitrogen-cooled cryostat and excited by the 514.5 nm Ar-ion laser line at a power density of 6 kW/m².

Figure 1 shows the PL spectrum, measured at 80 K, of a sample codoped with boron and annealed for 1 min. Similar spectra were also observed after 5 and 15 min anneals from samples codoped with boron. The strongest emissions occurred in the 2 μm region. The peak intensity of the main 2 μm emission, for this particular sample, is 13 times higher than the most intense line in the 1.2 μm region seen in the same spectrum. The 1.2 μm emissions, owing to the $^3H_5\text{--}^3H_6$ Tm^{3+} internal transitions, and the 1.13 μm silicon band-edge emission have been reported elsewhere and so will not be discussed further here [3,4,6]. In contrast, Tm^{3+} -related transitions were not observed from samples implanted with Tm only but otherwise identically processed and measured.

Luminescence intensity varied with annealing time and the brightest PL was measured from samples annealed for the shorter times, 1 and 5 min. Over 20 transitions can be distinguished and are listed on Table 1. The luminescence quenched as the temperature increased, but a sharp transition at 1995 nm and at least six other peaks can still be clearly identified at 300 K, as shown in Fig. 2. For the samples codoped with boron, the spectra can be roughly separated into two regions, as shown in Fig. 3.

Fig. 1. Photoluminescence spectrum measured at 80 K of Tm^{3+} :Si sample codoped with B and annealed at 850 °C for 1 min.

Fig. 2. Photoluminescence spectrum of a $\text{Tm}^{3+}:\text{Si}$ sample annealed at 850 °C for 1 min measured at different temperatures. The 2016.2 nm peak quenches faster and is practically absent at room temperature, where the spectrum is dominated by a sharp peak centered at 1995 nm. The spectra have been displaced along the vertical axes for clarity.

Fig. 3. Expanded spectra detailing the main emissions observed at 80 K in the $\text{Tm}^{3+}:\text{Si}$ system (a) at the 1700–1960 nm range and (b) at the 1960–2080 nm range.

The first region, from 1700 to 1960 nm [Fig. 3(a)], consists of 13 lines separated by approximately 10 nm and with its main emission at 1805.6 nm, plus five relatively weak lines (~ 1860 – 1890 nm) separated by irregular intervals varying from 10 to 23 nm; the second, from 1890 to 2100 nm [Fig. 3(b)], consists of three main transitions peaked at 1987.5, 1997.5 and 2016.2 nm.

We attribute the luminescence in the 1.7–2.1 μm range to the transitions between the Tm^{3+} first excited state and the ground state. The Tm^{3+} first excited state lies around 2.0 μm and is variously denoted in the literature by either 3F_4 or 3H_4 , owing to the mixing of the 3F_4 , 3H_4 , and 1G_4 states by the spin-orbit interaction [7,8]. The transitions identified here have been previously observed in crystals [9–11] and also in GaAs and GaInP [12]. Table 1 summarizes the main peaks identified in other systems as well as in Si (this work). The Tm^{3+} first excited state has a degeneracy of 9 and the ground state 13, giving a maximum number of possible transitions of 117. Previous work on the same samples looking at the 3H_5 – 3H_6 transitions [3] indicated that the symmetry is primarily tetragonal, which would give four excited state multiplets and six ground state multiplets—a maximum of 24 transitions. The Stark splitting of the excited state multiplets is around 6 meV, so at the high measurement

Table 1. List of the Main Transitions, in nm, Identified in the $\text{Tm}^{3+}:\text{Si}$ System (This Work, at 80 K and 300 K) as Well as Previously Reported Transitions from [9] ($\text{CaWO}_4/77$ K), [10] ($\text{KCaF}_3/15$ K), [11] (Yttrium Scandium Gallium Garnet/77 K), and [12]

Si 80 K	Si 300 K	[9]	[10]	[11]	[12] ^a	[12] ^b
					1709	
1732						
1742	1739				1745	
1749					1754	
	1753					
1763		1756		1760		
1774		1775	1774	1779	1777	
1784	1781	1786			1782	
1796		1797		1791		
1806	1806	1807		1812	1810	
1819			1819			
1825				1822	1826	
1835		1831	1837			1835
1846	1843				1845	1845
1856		1859		1857	1852	
	1864			1862		
1881	1884		1875	1871	1880	1880
		1893		1891		
1899			1900		1898	1898
		1911		1908		
1922	1917	1916			1917	1917
1932	1928		1935			
	1937					
1954	1956			1958	1961	
1971			1965	1977		
1987	1995					1989
1997				1995		2000
2016	2013		2005	2015	2010	
2074	2045					
2107						

^a(GaAs/4 K)

^b(GaInP/4 K)

temperature of 80 K, we would expect to see contributions from all of the excited state levels in proportion to their thermal population, as observed here. It is also possible that some distortion of the Tm^{3+} ion from the simple T_d site to a site of lower symmetry has occurred [3].

To the best of our knowledge, this is the first report of luminescence in the $2\ \mu\text{m}$ region in silicon doped with Tm. This is of particular interest, as the $2\ \mu\text{m}$ thulium emission is known to support lasing. The main emissions identified here (1773.7, 1805.6, 1835.0, 1997.5, and 2016.2 nm) have all been observed in other systems. The small differences between the peak positions measured here and work reported elsewhere (see Table 1) are attributed mainly to the different crystal host structures. Thulium-related luminescence is detected only in samples codoped with boron. The controlled implantation and postimplant anneal conditions of boron in silicon induce the formation of dislocation loops that can minimize or suppress the luminescence thermal quenching. Maximum light emission efficiency occurs when the loops' density is maximum [13]. For the B fluence and anneal temperature reported here, this is achieved for 1–5 min anneal, so longer anneal times can reduce the PL intensity.

Room-temperature photoluminescence at $2\ \mu\text{m}$ from silicon structures fabricated using standard processes is in itself a significant result. Silicon, while it is the material of choice for most microelectronic applications, has an indirect bandgap and so is considered unsuitable as an optical emitter. Here we demonstrated that by combining the introduction of an RE element into silicon, to provide wavelength tuning, with the dislocation engineering approach, which enhances high-temperature luminescence, room-temperature luminescence at a predetermined wavelength can be achieved. Tm^{3+} can be excited electrically in silicon via bandgap recombination

and Tm:Si LEDs have already been demonstrated. Tm^{3+} possesses intrinsic gain and optically pumped thulium lasers operate in the $2\ \mu\text{m}$ spectral region. If sufficient gain can also be demonstrated in Tm^{3+} :Si, the development of a room-temperature electrically pumped laser could become a realistic possibility.

We acknowledge the European Research Council for financial support under the FP7 for the award of the ERC Advanced Investigator grant SILAMPS 226470.

References

1. K. Scholle, S. Lamrini, P. Koopmann, and P. Fuhrberg, in *Frontiers in Guided Wave Optics and Optoelectronics*, B. Pal ed. (INTECH, 2010), pp. 471–500.
2. G. S. Pomrenke, E. Silkowski, J. E. Colon, D. J. Topp, Y. K. Yeo, and R. L. Hengehold, *J. Appl. Phys.* **71**, 1919 (1992).
3. M. A. Lourenço, R. M. Gwilliam, and K. P. Homewood, *Appl. Phys. Lett.* **92**, 161108 (2008).
4. M. A. Lourenço, C. Opoku, R. M. Gwilliam, and K. P. Homewood, *Opt. Mater.* **32**, 1597 (2010).
5. L. F. Johnson, J. E. Geusic, and L. G. Van Uitert, *Appl. Phys. Lett.* **7**, 127 (1965).
6. W. L. Ng, M. A. Lourenço, R. M. Gwilliam, S. Ledain, G. Shao, and K. P. Homewood, *Nature* **410**, 192 (2001).
7. D. S. Pytalev, S. A. Klimin, and M. N. Popova, *J. Rare Earths* **27**, 624 (2009).
8. H. P. Jenssen, A. Linz, R. P. Leavitt, C. A. Morrison, and D. E. Wortman, *Phys. Rev. B* **11**, 92 (1975).
9. L. F. Johnson, *J. Appl. Phys.* **34**, 897 (1963).
10. C. Y. Chen, W. A. Sibley, D. C. Yeh, and C. A. Hunt, *J. Lumin.* **43**, 185 (1989).
11. M. D. Seltzer, J. B. Gruber, M. E. Hills, G. J. Quarles, and C. A. Morrison, *J. Appl. Phys.* **74**, 2821 (1993).
12. K. Pressel, J. Weber, C. Hiller, D. Ottenwälder, W. Kürner, A. Dörnen, F. Scholz, K. Locke, D. Wiedmann, and F. Cordeddu, *Appl. Phys. Lett.* **61**, 560 (1992).
13. M. Milosavljević, M. A. Lourenço, G. Shao, R. M. Gwilliam, and K. P. Homewood, *Appl. Phys. B* **83**, 289 (2006).