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Erbium-doped optical waveguide materials based on Si nanocrystals formed by metal vapour vacuum arc ion implantation

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Abstract

Dual implantation of erbium and silicon into thermally grown SiO_2 film on Si was performed using a metal vapour vacuum arc ion source; this was followed by rapid thermal annealing at 500–1100 °C for 20 s. 1.54 μm photoluminescence (PL) was observed at 77 K. Rutherford backscattering spectrometry shows that Er ions mainly distribute within 80 nm of the surface. The highest Er peak concentration obtained exceeded 5×10^{21} cm^{-3}, which is the highest Er concentration reported in Si-based materials. Transmission electron microscopy demonstrates that nanocrystalline silicon (nc-Si) embeds in SiO_2 matrices. The Er^{3+} excitation energy is obtained from the electron–hole pairs nonradiatively combining at defects and impurities in SiO_2 matrices or at the interface of the nc-Si/SiO_2 (or c-Si/SiO_2), and energy transferring to Er^{3+} ions results in 1.54 μm light emission. The dependence on the Si-ion dose and annealing temperature of the PL intensity has also been investigated.

1. Introduction

The achievement of efficient light emission from Si is an important step towards the development of Si-based optoelectronics [1]. Among the several approaches, using Er-doped Si has been recognized as one of the most attractive and promising because its 1.54 μm emission coincides with the low-attenuation region of silica optical fibres [2, 3]. Recently, light emission from Er-doped porous Si (p-Si) [1], Si-rich silica thin films [4], and nanocrystalline silicon (nc-Si) in silica matrices have also been demonstrated [5]. To make a useful Er-doped optical device based on Si-based materials, it is necessary to use a high Er concentration, which involves cooperative interaction between neighbouring Er atoms. Cross-relaxation and energy migration between the Er^{3+} ions quenches the pumping efficiency. Furthermore, the lifetime

of the radiative transition (∼2 ms) exposes the excited Er ions to several nonradiative routes, e.g. a back-transfer process in which excited Er decays to the ground state and an electron from the Si valence band is promoted to the defect level. The presence of these de-excitation processes has hampered the achieving of room temperature (RT) light emission for a long time. However, a significant reduction of the back-transfer strength can be achieved using Si-based materials with a band gap larger than that of crystalline Si (c-Si), such as nc-Si embedded within SiO_2 [5, 6]. Moreover, a high Er concentration ranging from 10^{20} to 10^{21} cm^{-3} can be attained and nanometre structure can be formed by metal vapour vacuum arc (MEVVA) ion implantation, followed by thermal annealing [7].

2. Experiment

Samples were prepared through dual implantation of Si and Er ions into thermally oxidized Si (oxide thickness around 210 nm). The MEVVA ion implantations of Si and Er were performed in two stages with an extraction voltage of 45 kV. Firstly, (1–15) $\times$ 10^{17} cm^{-2} Si^+ ions were implanted into SiO_2 films with an ion flux of 85 μA cm^{-2}; with so large an ion beam current the substrate temperature was elevated and this allowed substrate annealing to occur, typically at temperatures of ∼400 °C. Secondly, (1–40) $\times$ 10^{16} Er^+ cm^{-2} ions with an ion flux of 5 μA cm^{-2} were implanted. Lastly, samples were annealed at 500–1100 °C in a flowing Ar atmosphere for 20 s. This treatment has been shown to produce Si nanocrystals. Er and Si concentration depth profiles were measured using Rutherford backscattering spectrometry (RBS) on a 2 $\times$ 1.7 MV tandem accelerator with normally incident 2.0 MeV $^4He^+$ beams at a scattering angle of 165°. The transmission electron microscope (TEM) images were obtained using a Hitachi H-600 electron microscope operated at 100 kV. The photoluminescence (PL) measurement was carried out using the 441.6 nm line of a He–Cd laser as the light source and a single-grating monochromator. A liquid-nitrogen-cooled Ge detector was used to detect the infrared spectrum. PL measurements were performed at 77 K and RT.

3. Results and discussion

Figure 1 shows the RBS measurements of the samples containing 5 $\times$ 10^{17} Si cm^{-2} and various doses of Er ions. It should be noted that there are three charge states, 1^+, 2^+ and 3^+, for Si and Er ions in the MEVVA ion source with corresponding particle flux fractions of 63, 35 and 2% for Si ions and 2, 63 and 35% for Er ions, respectively. The implantation conditions are equivalent to a triple-energy implantation at energies of 45, 90 and 135 keV. Therefore, Er concentration profiles in the SiO_2 layers are quite different from the Gaussian concentration–depth profile induced by a single-energy ion implantation. The quasi-symmetrical concentration profile of Er is due to the quasi-equilibrium partial sputtering [8]. The Er peak concentrations for 1 $\times$ 10^{16}, 5 $\times$ 10^{16}, 1 $\times$ 10^{17}, 2 $\times$ 10^{17}, 3 $\times$ 10^{17} and 4 $\times$ 10^{17} Er cm^{-2} implantations of silica thin films are 0.9, 8.0, 9.4, 15.3, 13.3 and 13.0 at.% respectively. Most Er ions distribute within 80 nm of the surface. The implantation also yields an approximately Gaussian depth distribution of excess Si in the SiO_2 film, with peak concentrations of 11.1, 13.0 and 16.4 at.% for 5 $\times$ 10^{17}, 1 $\times$ 10^{18} and 1.5 $\times$ 10^{18} Si cm^{-2} implantation in silica films, respectively.

Figure 2 shows TEM images of 210 nm silica thin films implanted with Si and Er. High-density isolated nanoparticles appear on the surface of the sample implanted with 1 $\times$ 10^{16} Er cm^{-2}; XRD and RHEED measurements confirm that most of the nanoparticles are crystalline Si. HRTEM images show that Si nanocrystal has a particle diameter in the range 2.5–7.0 nm. Assuming an average (∼4 $\times$ 10^3 Si atoms) nanocrystal diameter of 4.8 nm, the nanocrystal concentration is estimated to be 10^{18}–10^{19} cm^{-3}. The defects and damage are

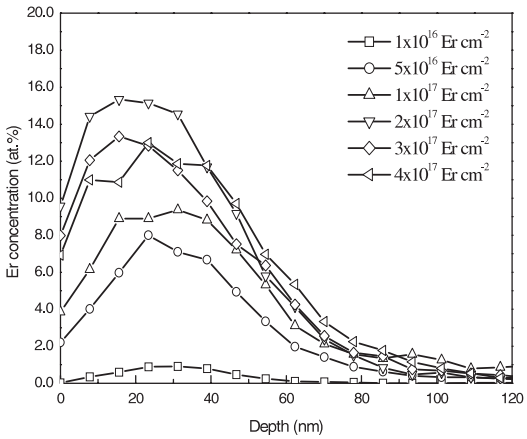

Figure 1. The RBS measurement of the Er concentration in SiO_2 thin films following dual implantation with Si and Er.

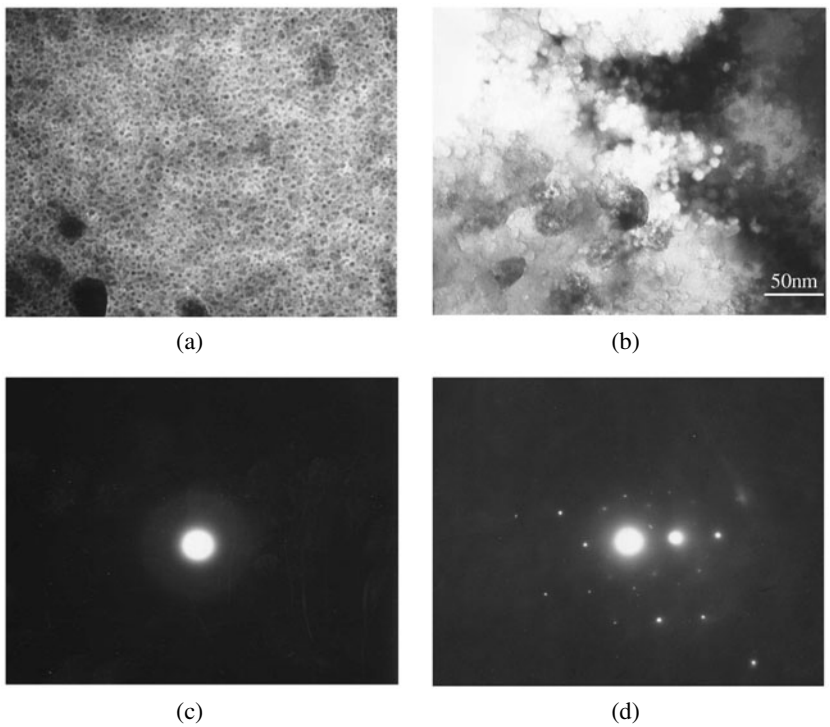

Figure 2. TEM images of samples implanted with 5×10^{17} cm^{-2} Si^+ and 1×10^{16} and 5×10^{16} cm^{-2} Er^+ annealed at 1000 °C for 20 s. (a) 1×10^{16} cm^{-2} Er^+; (b) 5×10^{16} cm^{-2} Er^+; (c) an electron diffraction pattern for samples (a); (d) an electron diffraction pattern for sample (b).

also caused in the surface by displacement processes after 1000 °C annealing for 20 s. This indicates that the mechanism of formation of these particles is growth rather than sputtering and surface migration, but strongly associated with the self-annealing effect induced by the high target temperature. On increasing the implanted Er-ion dose to 5×10^{16} cm^{-2}, the size

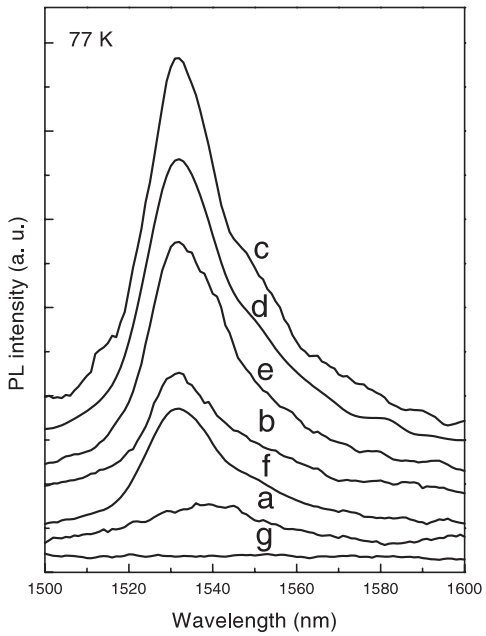

Figure 3. PL spectra of SiO_2 films containing nc-Si and Er at 77 K. The Er-ion dose and film thickness for all the samples are fixed at 1×10^{17} cm^{-2} and 210 nm, respectively, and the Si-ion dose is varied from 0 to 1.5×10^{18} cm^{-2}. (a) No Si; (b) 1×10^{17} cm^{-2}; (c) 3×10^{17} cm^{-2}; (d) 5×10^{17} cm^{-2}; (e) 8×10^{17} cm^{-2}; (f) 1×10^{18} cm^{-2}; (g) 1.5×10^{18} cm^{-2}.

of the particles and defects enlarges and becomes larger than that for the sample implanted with 1×10^{16} Er cm^{-2}. RTA releases the lattice stress induced by the ion bombardment, and some defects may be eliminated, but the RTA process cannot completely remove the defects and disorder.

Figure 3 shows 77 K PL spectra of films containing nc-Si and 1×10^{17} Er cm^{-2} as a function of Si-ion dose. For the sample not implanted with Si, we can see a very weak optical signal at 1.54 μm, which demonstrates that the optical cross-section for the intra-4f transition of Er^{3+} is rather small. The incorporation of nc-Si considerably enhances the effective Er^{3+} absorption cross-section; the implantation of 1×10^{17} Si cm^{-2} increases the intensity of the 1.54 μm luminescence by more than a factor of three with the same Er concentration. The Er^{3+} acts as an isolated ion luminescence centre. Excitation energy is obtained from the photocarriers generated in nc-Si and nonradiatively combined at defects and impurities in SiO_2 matrices or at the interface of the nc-Si/SiO_2. The intensity from the sample implanted with 3×10^{17} Si cm^{-2} is approximately ten times higher than that from the sample not containing nc-Si, and has a full width at half-maximum (FWHM) of 33 nm. However, the PL intensity begins to decrease when there is 5×10^{17} Si cm^{-2} implantation into the SiO_2 films. Moreover, a significant decrease of the PL is evident for the sample implanted with 1×10^{18} Si cm^{-2}, indicating that Er^{3+} ions locate in a predominantly Si environment. The PL is quenched when the Si-ion dose reaches 1.5×10^{18} Si cm^{-2}. We therefore speculate that for low concentrations of excess Si in SiO_2 films, enhanced Er^{3+} PL results from energy exchange between the nc-Si and Er. However, at high concentrations, the proportion of Er^{3+} lying within the Si clusters is sufficiently high that the PL yield is reduced.

Figure 4 shows PL spectra following Si and Er dual implantation into 90 nm silicon samples annealed from 500 to 1100 °C for 20 s. No clear 1536 nm light signal can be detected at 77 K

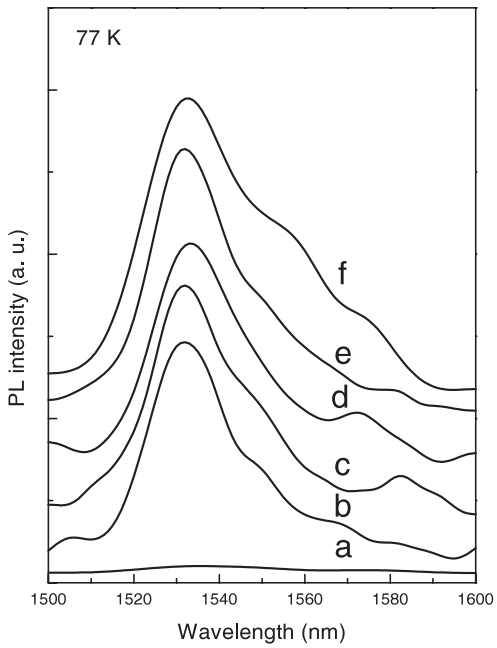

Figure 4. PL spectra of SiO_2 films containing nc-Si and Er at 77 K. The Er- and Si-ion doses for all the samples are fixed at 1×10^{17} and 5×10^{17} cm^{-2}, respectively, and the film thickness is 210 nm. (a) As-implanted; (b) 500 °C; (c) 700 °C; (d) 900 °C; (e) 1000 °C; (f) 1100 °C.

in the as-implanted sample. This implies that Er^{3+} is not optically active before annealing, and nc-Si structures do not come into being. The PL spectral shape for Er^{3+} does not change appreciably for annealing temperatures from 500–900 °C. Relatively good Er PL intensity was observed from samples annealed at 1000–1100 °C, which is thought to be attributable to a more efficient excitation due to the increased carrier lifetime in this temperature range of RTA. It should be noted that the minority-carrier lifetime in the Si host is a crucial factor in determining the Er excitation efficiency. From figure 2 we find that high-density nc-Si structure is formed upon RTA. And some defects are eliminated and disorder removed, which reduces the rate of occurrence of nonradiative transitions due to point defects or impurities. The formation of nc-Si significantly reduces the back-transfer strength because of it having a larger band gap than c-Si. If the annealing temperature and time continue to increase, this may favour nc-Si growth and Er recrystallization, resulting in reduction of the Er^{3+} PL yield. Most importantly, to attain optimum Er^{3+} light emission, it is necessary to carry out annealing at 1000–1100 °C for 20 s.

4. Conclusions

Samples of erbium-doped nc-Si embedded in silica films were fabricated by MEVVA ion implantation, followed by rapid thermal annealing at 500–1100 °C for 20 s. 1.54 μm PL was observed at 77 K. The highest Er peak concentrations obtained exceeded 5×10^{21} cm^{-3}, which is the highest Er concentration reported in Si-based materials. PL intensity first increases with the Si-ion dose increasing, then it decreases after the PL saturates at a certain ion dose. To achieve optimum Er^{3+} light emission, it is necessary to carry out annealing at 1000–1100 °C for 20 s.

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