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1.54 μm photoluminescence of Er-doped GeO_x thin films

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Amorphous Er-doped GeO_x alloys were prepared by evaporation on substrates maintained at 100 °C. Photoluminescence experiments were carried out in the visible and near-infrared ranges. The Er-related peak was observed at 1.54 μm at room temperature in the as deposited samples. The PL of erbium is characterized by a weak temperature quenching and by a decay time in the millisecond range. The luminescence of Er is a decreasing function of the annealing temperature. Undoped GeO_x layers showed a PL band at 800 nm, attributed to defects states, which disappeared when Er is introduced. The intense Er-related luminescence was assigned to an indirect excitation process from defects states to Er ions. © 2007 American Institute of Physics.

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Erbium has played an important role in the development of the optical communication technology in the last years because the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in the internal 4f shell of the trivalent Er^{3+} ion presents an emission at 1.54 μm (0.8 eV) which corresponds to the maximum transparency of the silica-based optical fiber. Er-doped thin films can be used to obtain planar optical amplifiers and many studies were focused on oxide glasses such as SiO_2 , phosphosilicate, or borosilicate glasses, or on ceramic thin film such as Al_2O_3 , Y_2O_3 , or LiNbO_3 , or on amorphous or crystalline silicon.¹

Studies on Er-doped crystalline silicon have shown that Er^{3+} ions can be efficiently excited through electron-hole pair recombination or by impact of energetic carriers.^{2,3} However, such systems present a strong temperature quenching which is due to Auger dissociation of electron-hole pairs and energy back transfer to silicon.⁴ This thermal quenching is strongly reduced when oxygen is coimplanted and the Er luminescence yield at room temperature is improved.⁵ In the presence of silicon nanocrystals (Si-nc), the Er-related photoluminescence (PL) is strongly improved. This effect is attributed to a strong coupling between Er^{3+} ions and Si-nc. The Er ions can then indirectly be excited by Si-nc that have an absorption cross section several orders of magnitude higher than that of direct Er excitation.^{6,7}

Contrary to the intense research that has been carried out on the Er-doped Si-based materials, there are very few reports on the luminescence from Er-doped Ge-based thin films. These materials are of interest from fundamental and applied points of view. For example, Er-doped SiGe alloys are interesting structures for active waveguide fabrication because the presence of Ge increases the refractive index.^{8,9} However, in Er-doped SiGe samples, a decrease in the PL intensity and a stronger temperature dependence were observed with increasing Ge content.¹⁰ Two papers have reported the Er-related PL in Ge and Er-doped SiO_2 thin films.^{11,12} In these works, the authors concluded to the probable existence of a coupling phenomenon from Ge nanoclusters

to Er ions, in a similar way with what happens with Si nanocrystals. Moreover, in the case of Er-doped Ge, it was shown that the oxidation of the layer improves the luminescence properties of Er.¹³ Indeed, the authors have shown that, in Er-doped nanocrystalline Ge prepared by evaporation, the 1.54 μm PL is only obtained after oxidation of the film by annealing in air at 500 °C. No energy transfer was clearly demonstrated in Er-doped GeO_x layers.

Our group has recently prepared GeO_x films by evaporation.^{14,15} With thermal annealing, these films present a phase separation inducing the appearance of Ge aggregates or Ge-rich areas in a GeO_2 matrix. The evolution of the infrared (IR) absorption and Raman spectrometries correlated to the PL experiments suggests that the PL originates in the presence of defects in the oxide matrix for annealing temperatures less than 350 °C and in the Ge aggregates for higher annealing temperatures. In this letter, we report on a study of Er-doped GeO_x thin films. It is shown that the luminescence at 1.54 μm can be observed in as deposited samples and in the annealed samples for annealing temperatures lower than 500 °C. The high luminescence is assigned to an energy transfer mechanism occurring between the electronic states located in the GeO_x band gap and the Er^{3+} ions. The PL disappears after apparition of Ge nanocrystals in GeO_x matrix.

The 200 nm thick films were obtained by evaporation of a GeO_2 powder from an electron beam gun. The base pressure was 10^{-8} Torr. The pressure increases during the evaporation until 3×10^{-6} Torr, due to partial decomposition of GeO_2 . Consequently, the films are substoichiometric and their composition, estimated by energy dispersive x-ray spectroscopy, is $\text{GeO}_{1.5}$. The silicon substrates were maintained at 100 °C. The deposition rate, controlled by a quartz microbalance, was 0.1 nm/s. For Er doping, the temperature of the effusion cell was around 1100 °C. The cell was calibrated by a quartz microbalance, allowing us to control the rare-earth content. The Er composition, defined by $C_{\text{Er}} = [\text{Er}]/[\text{Ge}] + [\text{O}] + [\text{Er}]$, is equal to 2.45%. After deposition, the films were annealed in a high-vacuum quartz tube with a tubular

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FIG. 1. Room-temperature PL spectra of Er-doped GeO_x alloys for different annealing temperatures T_a .

oven. The heating rate was $10^\circ\text{C min}^{-1}$. When the annealing temperature T_a was reached, this oven was pushed away and the films cooled naturally. Transmission electron microscopy has shown that the films remain amorphous for T_a lower than 600°C .

The PL in the range of 500–1700 nm was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. Both continuous-wave (CW) and time-resolved (TR) PL experiments were performed. For the CW experiments, the sample was excited by a 30 mW He–Cd laser using the 325 nm line. For the TR-PL experiments, the sample was pumped by the 355 nm line of a frequency-trippled YAG (yttrium aluminium garnet):Nd laser. The laser pulse frequency, energy, and duration were typically equal to 10 Hz, 50 μJ , and 20 ns, respectively. The response of the detection system was precisely calibrated with a tungsten wire calibration source.

Figure 1 shows the room-temperature 1.54 μm PL spectra for different annealing temperatures. These spectra correspond to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in the internal $4f$ shell of the trivalent Er^{3+} ions. Their shapes are very similar to that observed by Chen *et al.*¹³ for an Er-doped germanium films prepared by evaporation and annealed in air at 500°C for 1 h. The spectrum of the sample annealed at 300°C is identical to that of the as deposited sample. For higher annealing temperatures, the intensity of the PL peak decreases and the PL disappears for T_a equal to 500°C .

PL measurements at 77 K in the range of 500–1700 nm are represented in Fig. 2 for undoped and Er-doped samples (Fig. 2). For the as deposited undoped sample, the PL spectrum shows a very broad band between 700 and 1300 nm. The spectrum remains very similar for T_a less than 350°C . For higher annealing temperatures, this band disappears and another weaker and broad band appears with a maximum near 1400 nm. In a previous paper the PL in the visible range was attributed to radiative defects states in the band gap structure.¹⁴ These defects remain up to annealing temperatures equal to around 350°C . With annealing treatments at higher temperatures, there is a strong modification of the structure, characterized by the suppression of these defects and by the phase separation of the alloy with the appearance

FIG. 2. PL spectra at 77 K of GeO_x and Er-doped GeO_x alloys for as deposited samples (a) and for samples annealed at 450°C (b).

of Ge aggregates in a GeO_2 matrix. The PL band which appears around 1400 nm, corresponds to energies slightly higher than the band gap of germanium and could be assigned to confined Ge aggregates.

The PL spectra of the doped samples present the 1.54 μm Er-related PL peak. The intensity of the peak for the as deposited film is strong whereas the large band around 800 nm has disappeared, suggesting that an energy transfer between the defects states and the Er levels could exist. Only a band is visible at 980 nm corresponding to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition in the Er^{3+} ions. The sample annealed at 450°C shows a much weaker Er^{3+} PL peak, and the near-infrared band attributed to Ge aggregates is unchanged. Contrary to silicon, it seems that there is no energy transfer between the Ge aggregates and the Er^{3+} ions. In fact, the Si-nc present a PL band around 800 nm, which corresponds to the $^4I_{9/2}$ energy level of erbium, which explains the efficient energy transfer between Si-nc and Er^{3+} ions. It can be supposed that, in the germanium oxide alloys, such a resonance occurs from the energy of the defects present in the matrix for T_a lower than 350°C . Higher annealing temperatures lead to the disappearance of these defects and therefore of the coupling, which could explain the decrease of the Er-related PL peak intensity. For the sample annealed at 450°C , the PL band corresponding to the nanoclusters is very weak at 800 nm and the coupling with the $^4I_{9/2}$ energy level of erbium is unlikely. Moreover, for the erbium-doped sample, this band is unchanged, which is the proof that no coupling occurs. Moreover, due to the phase separation process induced by the annealing treatments, amorphous Ge aggregates appear and grow up. Consequently, the largest germanium clusters which have a band gap close to that of bulk germanium (0.66 eV at 300 K) could also contribute to the decrease of the intensity by absorption of the signal emitted by the Er^{3+} ions.

The time dependence of the 1.54 μm PL at room temperature is represented in Fig. 3 for an as deposited sample. The intensity decrease versus the time follows an exponential behavior. The PL decay time, equal to 1.7 ms, is very similar to the PL decay time of Er-doped Si-rich SiO_2 matrix.¹⁶

FIG. 3. Time dependence of the 1.54 μm PL for the Er-doped GeO_x as deposited sample.

The temperature dependence of the integrated intensity of the 1.54 μm Er-related PL peak and of the decay time are represented in Fig. 4. The decay time is equal to 3.5 ms at 4.2 K and it decreases slowly with temperature until the value of 1.7 ms at 300 K is reached. This decrease indicates that thermally activated processes occur in the material. These processes have also influence on the PL integrated intensity which decreases very slowly between 4.2 and 100 K and more rapidly between 100 and 300 K. The intensity is divided by a factor of 5 between 4.2 and 300 K. This temperature quenching is slightly greater than that observed for Er in SiO_2 containing Si-nc (Ref. 7) but it is, however, much smaller than that observed in crystalline silicon which

FIG. 4. Temperature dependence of the 1.54 μm PL integrated intensity ($\square$) and of the decay time (+) in the range of 25–300 K for the Er-doped GeO_x as deposited sample. The intensity values are normalized versus the intensity measured at 4.2 K.

presents a ratio greater than a factor of 100 in the range of 77–300 K.^{5,17} These different values suggest that thermally activated processes exist in Er-doped GeO_x . Their influence is comparable to that observed in SiO_2 containing Si-nc, but it is much weaker than that observed in bulk Si.

In summary, the 1.54 μm Er-related PL peak can be observed in Er-doped GeO_x alloys prepared by evaporation. The temperature quenching of the PL is weak, that allows us to obtain a high PL intensity at room temperature. The energy and decay time of this PL are very similar to that obtained in Er-doped Si-rich SiO_2 matrix. For the films annealed at temperatures lower than 350 $^{\circ}\text{C}$, the 1.54 μm PL intensity is strong. For higher annealing temperatures, the intensity of the Er-related peak rapidly decreases. A probable energy transfer mechanism from defect states in the band gap of the GeO_x matrix to the Er ions could be at the origin of the Er-related PL.

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¹A. Polman, J. Appl. Phys. **82**, 1 (1997).

²F. Priolo, G. Franzò, S. Coffa, and A. Carnera, Phys. Rev. B **57**, 4443 (1998).

³G. Franzò, F. Priolo, S. Coffa, A. Polman, and A. Carnera, Appl. Phys. Lett. **64**, 2235 (1994).

⁴F. Priolo, G. Franzò, S. Coffa, A. Polman, S. Libertino, R. Barklie, and D. Carey, J. Appl. Phys. **78**, 3874 (1995).

⁵S. Coffa, G. Franzò, F. Priolo, A. Polman, and R. Serna, Phys. Rev. B **49**, 16313 (1994).

⁶M. Fujii, M. Yoshida, Y. Kansawa, S. Hayashi, and K. Yamamoto, Appl. Phys. Lett. **71**, 1198 (1997).

⁷G. Franzò, V. Vinciguerra, and F. Priolo, Appl. Phys. A: Mater. Sci. Process. **69**, 3 (1999).

⁸A. J. Kenyon, Prog. Quantum Electron. **26**, 225 (2002).

⁹M. Q. Huda, A. R. Peaker, J. H. Evans, D. C. Houghton, and W. P. Gillin, Electron. Lett. **33**, 1182 (1997).

¹⁰E. Neufeld, A. Sticht, K. Brunner, G. Abstreiter, H. Holzbrecher, H. Bay, and Ch. Buchal, Appl. Phys. Lett. **71**, 3129 (1997).

¹¹C. L. Heng, T. G. Finstad, P. Storås, Y. J. Li, A. E. Gunnæs, and O. Nilsen, Appl. Phys. Lett. **85**, 4475 (2004).

¹²J. Skov Jensen, T. P. Leervad Pedersen, J. Chevallier, B. Bech Nielsen, and A. Nylandsted Larsen, Nanotechnology **17**, 2621 (2006).

¹³J. H. Chen, D. Pang, H. M. Cheong, P. Wickboldt, and W. Paul, Appl. Phys. Lett. **67**, 2182 (1995).

¹⁴M. Ardyanian, X. Devaux, H. Rinnert, and M. Vergnat, Appl. Phys. Lett. **89**, 011902 (2006).

¹⁵M. Ardyanian, H. Rinnert, and M. Vergnat, J. Appl. Phys. **100**, 113106 (2006).

¹⁶D. Pacifici, G. Franzò, F. Priolo, F. Iacona, and L. Dal Negro, Phys. Rev. B **67**, 245301 (2003).

¹⁷P. G. Kik, M. J. A. de Dood, K. Kikoin, and A. Polman, Appl. Phys. Lett. **70**, 1721 (1997).