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Resonant excitation of Er ion luminescence in a nanocrystalline silicon matrix

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Abstract. The luminescence of amorphous silicon layers either implanted with Er or co-implanted with Er and O has been studied by photoluminescence (PL) and cathodoluminescence (CL) in the scanning electron microscope. Annealing in nitrogen causes the formation of oxide species and Er-Si complexes or precipitates as well as spectral changes in the visible and infrared ranges. The main CL emission takes place in the visible range while PL spectra reveal intense visible and infrared emission. CL spectra show blue-violet, or green, emission bands whose relative intensities depend on the post-implantation annealing temperature. The PL spectra show a blue-violet band with a series of lines in the violet region related to phonon assisted transitions as well as different emission bands in the range 1200–1500 nm. The influence of the annealing-induced structural changes on the observed spectra is discussed.

PACS. 61.72.Tt Doping and impurity implantation in germanium and silicon – 78.55.-m photoluminescence, properties and materials

1 Introduction

The luminescence of Er containing Si has been often investigated in the past years due to the wide interest in integrating light emitting silicon in the available silicon technology. Due to the low diffusivity of Er in Si, Er implantation appears as an efficient way to dope Si with Er [1,2] but the luminescence achieved is normally rather low. Certain thermal treatments and the presence of co-implanted elements contribute to enhance the luminescence efficiency. In particular, oxygen is a codopant which has been found to increase the Er emission at 1.54 μm in silicon, e.g., [3] and whose interaction with Er has been previously investigated [4–6]. In addition to effects due to impurities, the structure of the host matrix influences the Er luminescence efficiency in Si. The effect of incorporation of Er in silicon has been investigated for crystalline, amorphous, nanocrystalline or mixed amorphous-nanocrystalline host material. The latter system often corresponds to the case of nominally amorphous substrate after the recrystallization which takes place during ion implantation. Aldabergenova *et al.* [7] have discussed the microscopic nature of the characteristic infrared Er emission in amorphous-nanocrystalline silicon and have pointed out the possible advantages of using amorphous host for luminescence enhancement. In the present work the luminescence of amorphous silicon implanted with Er and O ions and its evolution during different thermal treatments has been investigated. In particular, the influence of the excitation conditions on the resulting luminescence spectra and the appearance of phonon assisted de-excitation processes has been analysed. Previous work on Er doped silicon prepared by deposition of erbium oxide layers [8] showed that CL (excited by the electron beam in a scanning electron microscope) favours emission in the visible range as compared with photo-excited luminescence which shows mainly emission in the infrared range.

2 Experimental

Amorphous silicon films with a thickness of about 2 μm were obtained by low-pressure chemical vapour deposition on p-type (100) silicon wafers at 570 °C and a pressure of 0.4 torr. The films were implanted with 200 keV ^{166}Er ions/cm^2 respectively. The implanted samples were annealed at temperatures of 600 °C, 750 °C and 900 °C respectively for half an hour in nitrogen atmosphere and slowly cooled down to room temperature. Due to the low penetration depth of the ions, grazing angle X-ray diffraction measurements were performed. All the samples were observed at 90 K, in a Hitachi S2500 SEM in the CL mode of operation, at an accelerating voltage of 25 kV.

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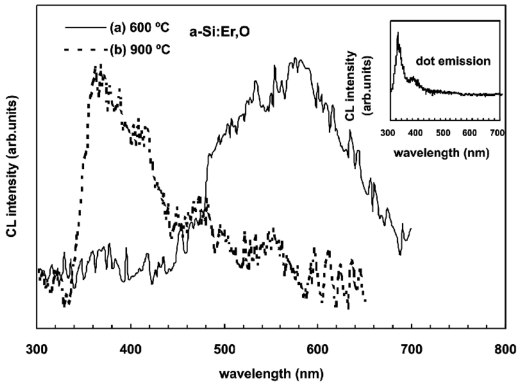

Fig. 1. CL emission spectra at 90 K of a-Si:Er, O sample after annealing at 600 °C and 900 °C with the dominant emission at 580 nm and 360–370 nm respectively. The inset shows CL spectrum recorded on a luminescent precipitate with the dominant emission in the 300–400 nm range.

Visible light was detected using a Hamamatsu R-928 photomultiplier, and a cooled ADC germanium detector was used in the near infrared. CL spectra were recorded by using an Oriel 78215 computer controlled monochromator or, in the visible range, with a CCD camera with a built-in spectrograph (Hamamatsu PMA-11). An Edinburgh Instruments CD-900 spectrometer was used for the PL measurements, with a 10 K closed-cycle helium cryostat to cool the samples. He-Cd (325 nm, 50 mW), and Ar-ion (488 nm, 20 mW), lasers were used as excitation sources.

3 Results and discussion

Annealing the implanted samples causes the formation of precipitates appearing as protruding surface features whose size, typically of the order of several microns, and number, increase with the annealing temperature. XRD measurements show the presence of diffraction peaks corresponding to Er_2O_3 and to Er-Si compound. The best fit for the latter compound corresponds to Er_5Si_3. Previous SEM-CL microscopy observations of these samples revealed that most of the precipitates present an intense luminescence band in the violet-blue range peaked at about 360–370 nm [9] while CL emission of the unimplanted amorphous layers presented a weak blue emission attributed to nanocrystals embedded in the amorphous matrix [10,11].

After the 600 °C anneal, only the samples implanted with Er and O, labelled a-Si:Er,O, show a clear increase of the CL emission with the appearance of a 580 nm luminescence band (Figure 1, solid line). After annealing at 900 °C the spectra of the a-Si:Er:O samples show a violet-blue band (Figure 1, dashed line) instead of the 580 nm emission while in the samples implanted only with Er, labelled a-Si:Er, the emission band is centered at about 440 nm [9]. The CL spectrum recorded on a luminescent precipitate shows the emission more concentrated in the range 300–400 nm (Figure 1, inset). The CL emission in the near infrared range is too weak to record spectra in the a-Si:Er samples even after annealing at 900 °C. Figure 2 shows the infrared CL spectrum of an a-Si:Er, O sample annealed at 900 °C. Similar spectra but with lower intensities were recorded after 750 °C annealing, while emission of the samples annealed at 600 °C was too low for spectra to be recorded.

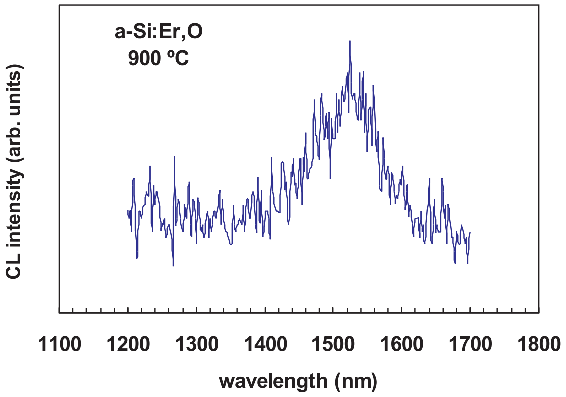

Fig. 2. Infrared CL spectrum at 90 K of a-Si:Er, O sample annealed at 900 °C.

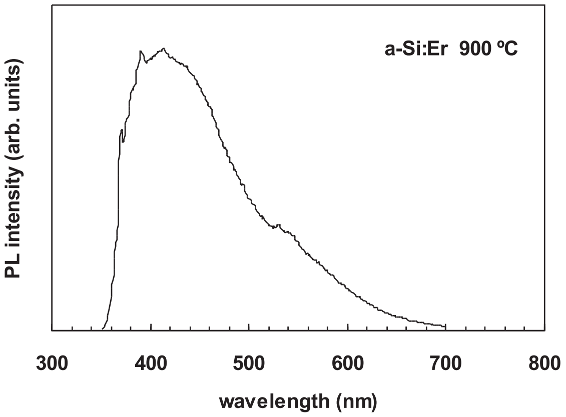

Fig. 3. PL spectrum at 10 K of a-Si:Er, sample annealed at 900 °C, recorded under excitation with He-Cd (325 nm) laser.

PL in the visible range consists of a blue band observed in all annealed samples by excitation with the He-Cd (325 nm) laser. Figure 3 shows the spectrum of an a-Si:Er sample annealed at 900 °C. The a-Si:Er, O samples annealed at 600 °C show a somewhat broader PL band (Figure 4) whose intensity was found to depend markedly on the sample region probed. We attribute this effect to the inhomogeneous distribution of luminescent dots revealed by CL microscopy, discussed in [9].

Infrared PL spectra have been found to depend markedly on the thermal treatment. Samples annealed at 900 °C show the erbium emission band at about 1540 nm

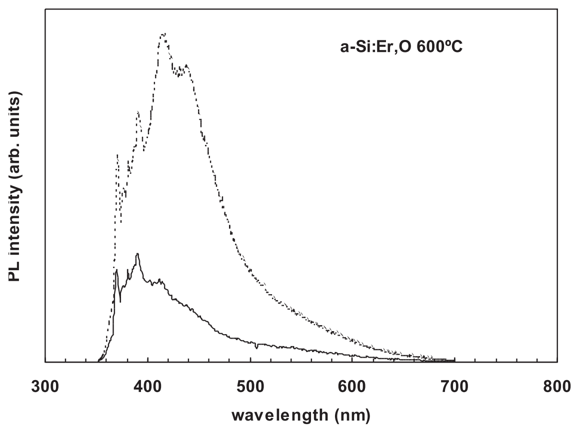

Fig. 4. PL spectra at 10 K of a-Si:Er, O after annealing at 600 °C corresponding to different areas in the sample. The excitation was with He-Cd (325 nm) laser.

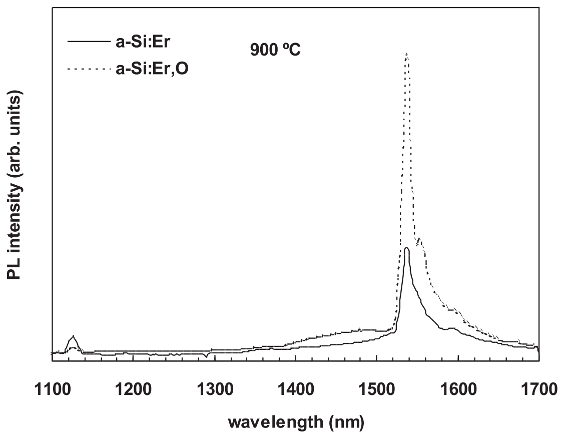

Fig. 5. Infrared PL spectra at 10 K of a-Si:Er and a-Si:Er, O annealed at 900 °C, recorded during excitation with Ar-ion (488) nm laser.

with a higher intensity in samples implanted with Er and O than in those implanted only with Er. Figure 5 shows the PL spectra of the Er and O implanted sample. The samples annealed at 600 °C show a more complex IR spectrum with several peaks in the range 1200–1500 nm in addition to the 1540 nm band which in this case is not the dominant emission (Figure 6). The spectra shown in Figures 5 and 6 were recorded during excitation with the 488 nm line of the Ar-ion laser. This leads to a higher luminescence intensity than the excitation with the 325 nm He-Cd line.

Previous CL results [9] showed the precipitates as light emitting structures, with the emission band peaked in the violet-blue region. The process of precipitate formation is more developed in the samples doped with Er and O, after the 900 °C annealing temperature. The average size of the Er_5Si_3 complexes is about 10 mm [9]. The CL peaks associated with the local excitation of a precipitate (Figure 1, inset) appear well resolved, and do not show a clear structure of emission lines. On the contrary, excitation with photons of 325 nm induces successive transitions, step-like structures, indicating the existence of phonon-assisted transitions. The multi-peak structure appears in the 370–390 nm region and is present in the a-Si:Er, O, a-Si:Er, and c-Si:Er implanted samples. The largest PL emission is observed for the a-Si doped only with Er and treated at 900 °C and corresponds with the maximum occurrence of Er-Si precipitates. The formation of Er-Si complexes has been investigated by Eaglesham et al. [12] and Alder et al. [13]. Precipitates of $ErSi_2$ with platelet morphology and dimensions of 100–300 Å were observed in Er implanted crystalline silicon and an increase of the 1.54 μm PL emission in the presence of precipitates was reported [12]. A structure of Er_3Si_5 epitaxial silicide precipitates has been also reported [14]. Our low temperature PL measurements presented in Figures 3 and 4 show a multi-peak structure on the high energy side of the band indicating the existence of phonon assisted de-excitation processes in the violet region, with phonon energy of 47 meV. While some of the transitions appear in the PL spectrum of the a-Si:Er, O implanted sample treated at 900 °C, the multi-peak structure appears better resolved and the differences among the peaks intensity are more pronounced in the spectrum of the a-Si:Er, O sample treated at 600 °C presented in Figure 4. In this sample the precipitation process is less developed and the precipitate structure was not detected by XRD.

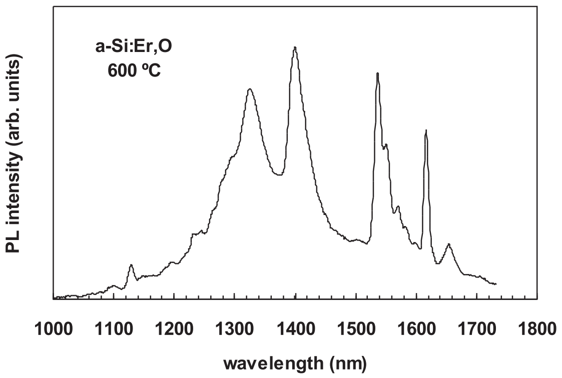

Fig. 6. Infrared PL spectra at 10 K of the samples annealed at 600 °C.

Kanemitsu [15] reported on phonon-assisted de-excitation processes in silicon nanoparticles, with transverse acoustic and transverse optical phonon energies of 18.5 and 57.5 meV respectively. Although the phonon energy in our experiment is of the order of the latter value, the presence of phonon- assisted transitions in our PL spectrum of crystalline silicon implanted with erbium (not shown), suggests that the process is not correlated with the silicon nanocrystallites, which possibly grow during the thermal treatment of the a-Si matrix. Since the CL emission associated with the presence of precipitates is not present in the spectrum of a-Si:Er, O treated at 600 °C, but the phonon assisted transitions are observed in the PL spectrum, the phonon related processes are more likely correlated with the Er-Si or Er-Er bonds, than with an extended precipitate structure. Short-range arrangements of Er in silicon, generating Er-luminescent centers, were seen to occur during solid phase epitaxy of Si co- implanted with Er and O [16]. Citrin *et al.* [17] reported that the formation of a Si:Er defect structure, resembling $Er_2Si_{1.7}$ is energetically favoured in Si, albeit with a low optical activity. Nonradiative de-excitation processes of Er in Si was proposed by Franzo *et al.* [18], to take place in an Er-Si system. This leads us to propose that Er-Er bond structures involving several Er atoms, and possibly O, should be considered to account for the observed phonon-assisted radiative recombination process in our experiment.

The process of phonon assisted radiative de-excitation was observed only under excitation with photons of 325 nm. The PL emission in the visible region was not detected using excitation with photons of 488 nm wavelength, then a resonant excitation process of Er-Er structures seems to be activated. The resonant energy transfer from the 325 nm photons used for excitation is relaxed through several acceptor-like energy levels. The less selective character of CL excitation, and the higher temperature (78 K) in the CL measurements results in phonon-assisted radiative de-excitation peaks [9] which are less well-resolved.

The selective character of PL excitation results in the appearance of emission peaks in the near infrared region, observed under excitation with photons of 488 nm wavelength but not with 325 nm photons. Infrared emission from the Er centers shows different emission bands. The 1540 nm peak, corresponding to the Er^{3+} intra-4f transitions involving the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$ appears well resolved in all samples with higher intensity in the samples co-doped with O and treated at 900 °C, Figure 5b. The effect of co-implanted oxygen in the formation of optically active centers is well known. The PL infrared spectrum of a-Si doped with Er and O and treated at 600 °C, is shown in Figure 6. After this treatment, the complexity of the PL infrared spectrum shows that the implanted matrix adopts a complex structure, with several different centers associated with Er. The peaks that appear well resolved, are situated at 1300, 1400, 1540, 1610 and 1630 nm respectively and most of the emission appears in the 1200–1500 nm region. CL spectra of Er oxides grown on different silicon substrates show a broad band situated at 1250–1300 nm, attributable to a defect involving oxygen [19]. The presence of an emission band at about 1310 nm in the spectrum of a-Si:Er, O treated at 600 °C (Figure 6), supports the hypothesis of a Er-O complex as the origin of this emission band. XRD confirms that Er and O co-implanted samples contain Er_2O_3. These samples also show a CL 580 nm peak characteristic of an erbium oxide phase. Michel *et al.*, [1], reported a strong PL band around 1400 nm from crystalline silicon implanted with Er and treated at 600 °C, possibly due to a remaining defect in the partially-recovered matrix at this temperature. In passing, we observed a poorly-resolved, step-like structure in the region 1100–1300 nm, which could be attributed to phonon-assisted radiative transitions similar to those observed in the violet region.

The group of distinct peaks observed in the region 1540−1610 nm, is associated with Er^{3+} internal transitions. Stark splitting of the Er^{3+} PL peaks in the 1460–1610 nm region has been reported recently [7], the splitting of the 1540 nm emission line being attributed to the presence of oxygen in an optimal position around the Er. Although not all the emission peaks mentioned are coincident with those present in our PL spectra, the main emission line splitting induced by a certain structure of Er-O complexes seems to be possible.

4 Conclusions

In conclusion, we report phonon-assisted radiative transitions from Er precipitates grown in implanted a-Si and c-Si. Such radiative transitions appear as a step-like structure in the violet region of the PL spectra of amorphous and crystalline silicon. The phonon energy is 47 meV. The transitions were observed by 325 nm photons excitation. Phonon contribution could be observed in the infrared region, under excitation with 488 nm wavelength photons. Resonant energy absorption and phonon assisted radiative recombination take place from different Er related centers formed in a-Si matrix.

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References

1. J. Michel, J. L. Benton, R. F. Ferrante, D. C. Jacobson, D. J. Eaglesham, E. A. Fitzgerald, Y. H. Xie, J. M. Poate, L. C. Kimerling, J. Appl. Phys. **70**, 2672 (1991)
2. A. Polman, J. Appl. Phys. **82**, 1 (1997)
3. H. Przybylinska, W. Jantsch, Y. Suprun-Belevitch, M. Stepikhova, L. Palmetshofer, G. Hendorfer, A. Kozanecki, R. J. Wilson, B. J. Sealy, Phys. Rev. B **54**, 2532 (1996)
4. M. Suezawa, M. Sumino, Jpn. J. Appl. Phys. **33**, L1782 (1994)
5. A. Terrasi, G. Franz, S. Coffa, F. Priolo, F. D'Acapito, S. Mobilio, Appl. Phys. Lett. **70**, 1712 (1997)
6. U. Wahl, A. Vantomme, G. Langouche, J. G. Correia, J. Lumin. **80**, 303 (1999)
7. S. B. Aldabergenova, H. P. Strunk, P. C. Taylor A. A. Andreev, J. Appl. Phys. **90**, 2773 (2001)
8. E. Nogales, B. Méndez, J. Piqueras, R. Plugaru, A. Coraci, J. A. García, J. Phys. D: Appl. Phys. **35**, 295 (2002)
9. R. Plugaru, B. Méndez, J. Piqueras, T. J. Tate, J. Phys. Cond. Matter **14**, 13153 (2002)
10. J. Piqueras, B. Méndez, R. Plugaru, G. Craciun, J. A. García, A. Remón, Appl. Phys. A **68**, 329 (1999)

11. R. Plugaru, G. Craciun, N. Nastase, B. Méndez, A. Cremades, J. Piqueras, E. Nogales, J. Porous Mater. **7**, 291 (1999)
12. D. J. Eaglesham, J. Michel, E. A. Fitzgerald, D. C. Jacobson, J. M. Poate, J. L. Benton, A. Polman, Y. H. Xie, L. C. Kimerling, Appl. Phys. Lett. **58**, 2797 (1991)
13. D. L. Adler, D. C. Jacobson, D. J. Eaglesham, M. A. Marcus, J. L. Benton, J. M. Poate, P. H. Citrin, Appl. Phys. Lett. **61**, 2181 (1992)
14. R. Serna, M. Lohmeier, P. M. Zagwijin, E. Vlieg, A. Polman, Appl. Phys. Lett. **66**, 1385 (1995)
15. Y. Kanemitsu, J. Lumin. **83-84**, 283 (1999)
16. K. Nakashima, O. Eryu, H. Akiyama, Y. Maeda, H. Ebisu, Nucl. Instrum. Methods B **175**, 208 (2001)
17. P. H. Citrin, P. A. Northrup, R. Birkhahn, J. Steckl, Appl. Phys. Lett. **76**, 2865 (2000)
18. G. Franzo, F. Priolo, S. Coffa, J. Lumin. **80**, 19 (1999)
19. E. Nogales, B. Méndez, J. Piqueras, R. Plugaru, J. A. García, T. J. Tate, Mat. Res. Symp. Proc. **692**, 455 (2002)

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