Study of thermal treated a-Si implanted with Er and O ions

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Abstract
Visible luminescence of amorphous silicon layers either implanted with Er or
co-implanted with Er and O and subsequently annealed in nitrogen has been
investigated by cathodoluminescence (CL) in a scanning electron microscope.
Co-implanted samples show a more intense luminescence, which is revealed by
annealing at lower temperatures than the samples implanted only with erbium.
Thermal treatments cause the formation of erbium oxide as well as Er–Si
complexes or precipitates. Violet–blue luminescence has been found from
CL images and spectra to be related to Er–Si precipitates. Emission in the
green–red range is attributed to oxide species.

1. Introduction

The incorporation of rare earth elements into a silicon matrix and the study of the resulting
emission properties of the material is a subject of interest related to the possibility of integrating
light-emitting silicon into the available silicon technology. Previous works on incorporation of
Er in silicon include the use of crystalline [1–3], amorphous [4–6] or porous [7] host material.
Due to the low diffusivity of Er in Si, Er implantation appears to be a suitable way to effi-
ciently dope Si with Er [8, 9]. However, the luminescence efficiency achieved is still rather low
and is in general restricted to low temperatures. For this reason, the study of the implantation
conditions and the subsequent treatments necessary to obtain efficient luminescence in erbium-
implanted silicon is a subject of interest. In particular, thermal treatments and the presence
of co-implanted elements have a strong influence on the erbium-related luminescence. The
efficiency of luminescence emission associated with the intra-ionic Er^{3+} radiative transitions
depends on the mechanism of energy transfer from the host to the complexes formed by erbium
and the surrounding atoms [10, 11]. The complex formation is, to a large extent, determined
by the presence of codopants and the structure of the host matrix [8, 12]. Oxygen is one

possible codopant of erbium in silicon, which has been found to enhance the Er emission at 1.5 μm (e.g. [13]) and whose interaction with erbium in the silicon matrix has attracted attention [14, 15]. Luminescence from rare earth ions in semiconductor hosts is, however, not limited to the infrared range but with appropriate combinations of host matrix, co-doping and thermal treatments practically the whole infrared to ultraviolet range can be covered. Visible luminescence with different emission bands depending on the use of crystalline or amorphous substrates has been observed in Er-doped silicon samples obtained by deposition of erbium oxide layers [16, 17]. These works refer mainly to cathodoluminescence (CL) in a scanning electron microscope (SEM). This technique was found to favour emission in the visible range, unlike in photo-excited luminescence, probably due to the high excitation conditions in the SEM. In this work, Er and O ions have been implanted in amorphous and in crystalline silicon and the light emission after different thermal treatments has been investigated by CL. The formation of Er-related phases in the samples following implantation and annealing has been investigated by x-ray diffraction (XRD) and correlated with the luminescent behaviour of the samples.

2. Experimental details

Amorphous silicon films with a thickness of about 2 μm were obtained by low-pressure chemical vapour deposition (LPCVD) on p-type (100) silicon wafers at a temperature of 570 °C and a pressure of 0.4 Torr. The films as well as crystalline substrates were implanted with 200 keV ^{166}Er ions at doses of 5×10^{15} cm^{-2}. Some of the amorphous silicon layers were co-implanted with 200 keV Er ions and 40 keV ^{16}O ions at doses of 5×10^{15} and 10^{16} cm^{-2} respectively. The implanted samples were annealed at temperatures of 600, 750 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. In order to study the possible agglomeration of erbium, mapping of this element was carried out by x-ray wavelength dispersive spectrometry (WDS) in a Jeol JXA-8900 M superprobe. All the samples were observed in the CL mode of operation in a Hitachi S2500 SEM in the temperature range 80–300 K and at an accelerating voltage of 25 kV. For the detection of visible light, a Hamamatsu R-928 photomultiplier was used while for the near-infrared light a cooled ADC germanium detector was employed. The CL spectra were recorded either with the photomultiplier tube attached to an Oriel 78215 computer controlled monochromator or with a CCD camera with a built-in spectrograph (Hamamatsu PMA-11).

3. Results and discussion

The secondary electron mode of the SEM shows, in general, a flat homogeneous surface of the samples but in some areas a distribution of protruding surface features, hereinafter designated as dots, is observed. The appearance of the dots depends on the thermal treatment used, with an increasing number and higher size at higher annealing temperatures. Figure 1 shows the SEM image of a distribution of dots. X-ray microanalysis mapping of the samples in the SEM reveals a decrease of Si and an increase of Er content in the dots' area. For similar exposure times the contrast appears more clearly revealed in the Si map. The XRD measurements show the recrystallization of the amorphous silicon after annealing at 900 °C while no clear silicon peak was observed in the sample annealed at 600 °C. Diffraction peaks of Er_2O_3 and of the Er–Si compound have been detected in all the implanted and annealed samples. The best fit for the Er–Si compound corresponds to the presence of Er_5Si_3.
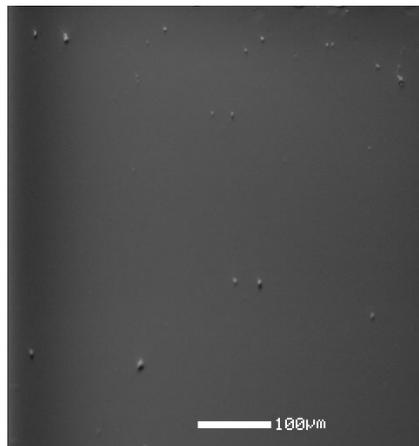
Figure 1. Secondary electron image of the sample a:Si:Er:O annealed at 900 °C.
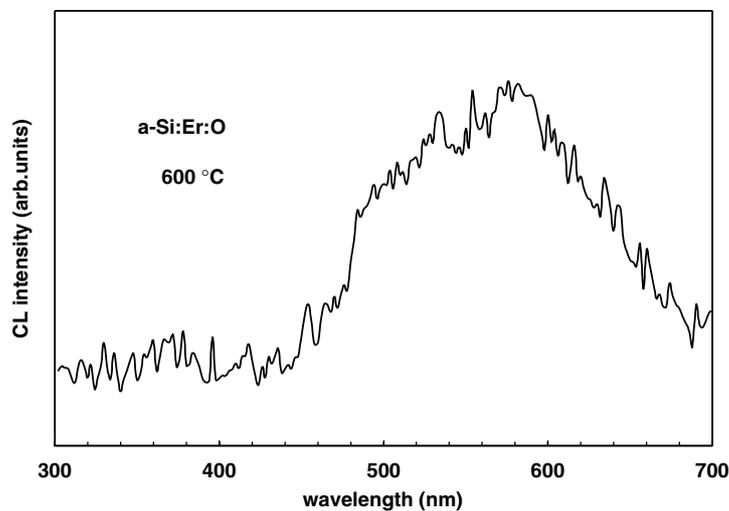

Figure 2. CL spectrum of the sample a-Si:Er:O annealed at 600 °C.

CL emission features of the unimplanted amorphous layers have been previously described [18, 19]. The layers present a weak emission mainly in the blue spectral range. This luminescence is explained by the presence of nanocrystals in the amorphous matrix. Implantation with boron ions was found to cause nanocrystal formation and the enhancement of a CL band centred at about 400–410 nm. Blue CL emission has also been observed in the samples implanted with Er or with Er and O ions without subsequent thermal treatment [17].

Annealing at temperatures up to 500 °C did not cause appreciable intensity or spectral changes. A thermal effect is first clearly observed as a luminescence intensity increase and appearance of a green emission band, after 600 °C annealing, only in the samples implanted with both Er and O ions. Figure 2 shows the spectrum of the a-Si:Er:O sample after the 600 °C annealing with a broad band peaked at about 580 nm. The spectra of the implanted samples after the 900 °C treatment are shown in figure 3. The sample a-Si:Er shows a broad band peaked at about 444 nm while the sample a-Si:Er:O presents a luminescence band in the violet–blue
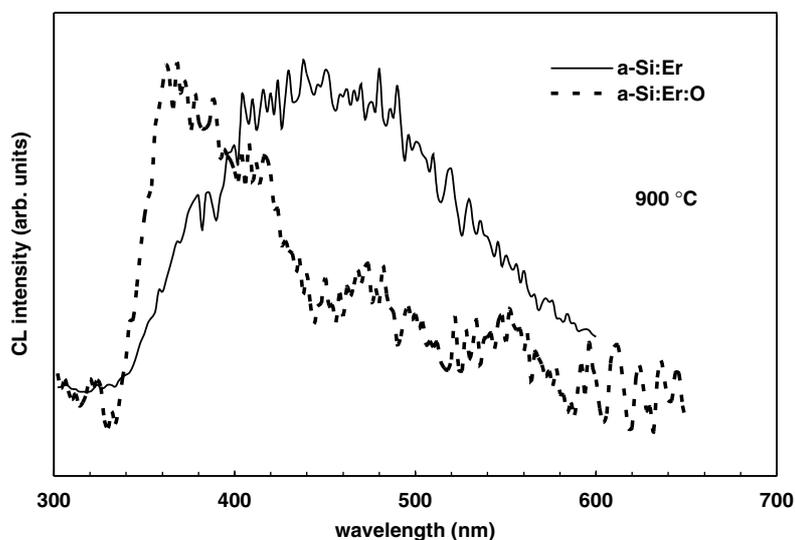
Figure 3. CL spectra of samples a-Si:Er and a-Si:Er:O annealed at 900 °C.
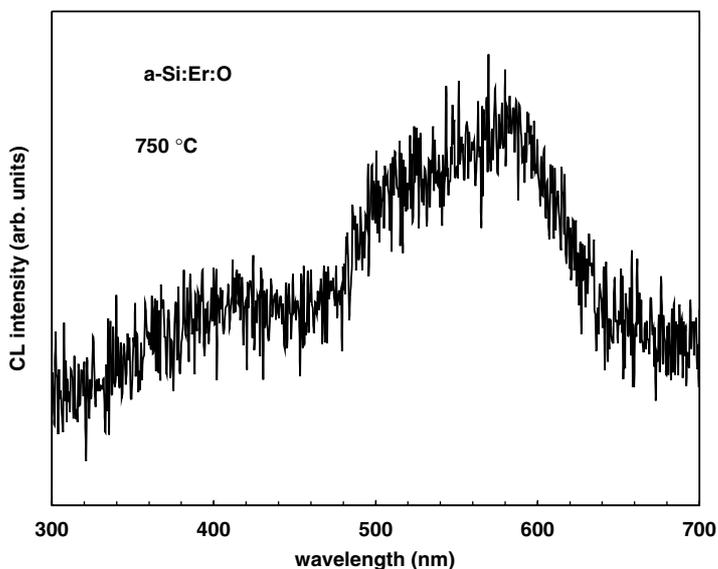

Figure 4. CL spectrum of the sample a-Si:Er:O annealed at 750 °C.

range peaked at about 360–370 nm. Spectra of the Er-implanted wafer annealed at 900 °C are qualitatively similar to those of the recrystallized amorphous sample with the same treatment. It has been previously found [16] that wafers after Er deposition and annealing in oxygen present a more intense red luminescence than amorphous layers after similar implantation and thermal treatment. Annealing at 750 °C produces in the a-Si:Er sample a similar effect to the 900 °C annealing, while in the a-Si:Er:O sample the CL spectrum shown in figure 4, is obtained. It can be observed that this temperature causes the appearance of weak emission in the blue region while the green band, which is the only emission after the 600 °C annealing, is still present.
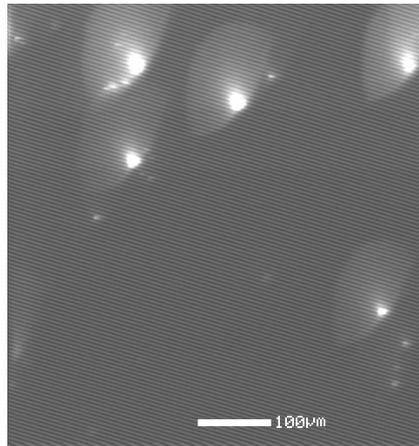
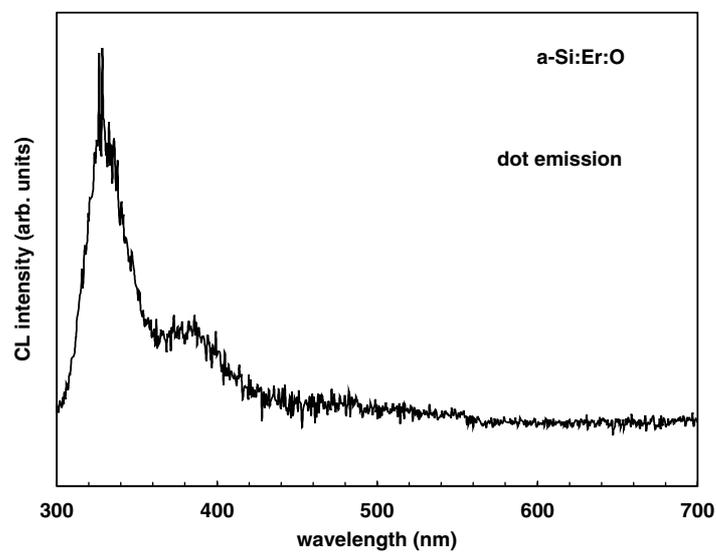**Figure 5.** CL image of the sample a-Si:Er:O annealed at 900 °C.

Figure 6. CL spectrum recorded at one of the bright spots shown in figure 5.

CL images show that luminescence distribution is inhomogeneous and that often the dots show an enhancement of total emission. Figure 5 shows the panchromatic CL image of a region with dots in the a-Si:Er:O sample. The CL spectrum recorded with the electron beam positioned on one of the dots is shown in figure 6. This spectrum shows that the blue emission detected in the spectra of figures 3 and 4 after annealing arises mainly from the precipitates included in the area on which the spectra are recorded. The large number and size of the precipitates in the a-Si:Er:O sample after the 900 °C annealing induces the dominant emission in the violet–blue range. Spectra recorded on precipitates after the 750 °C annealing also show blue emission. However, in this case the contribution of the precipitates to the total emission is low, as figure 4 shows. In addition to the above-described spectral features, it was found that co-implanted samples show a higher total luminescence than the samples implanted with erbium.

The present results show a different evolution of the visible luminescence of samples implanted with erbium and of those co-implanted with erbium and oxygen, during thermal treatments. In the latter case, annealing at temperatures of 600 °C produces intense luminescence in the green–red spectral range. The presence of oxygen clearly determines the appearance of this band, which agrees with previous CL observations of Er_2O_3 [16]. Erbium oxide was found to present two visible bands at 550 and 655–675 nm associated with Er ions, and the relative intensity of the green band was found to increase at low temperature. Both components are included in the broad band of the spectrum of figure 2 recorded at 90 K. This observation agrees with the presence of an erbium oxide phase detected by XRD in the annealed samples. After annealing at higher temperatures, the co-implanted samples show the appearance of a component in the blue range that appears as a shoulder after the 750 °C annealing and transforms into a violet–blue emission after the 900 °C annealing. The evolution of the luminescence correlates with the structural transformation during annealing as detected in the SEM by an increasing formation of precipitates with increasing annealing temperature and by the formation of an Er–Si compound observed by XRD. The association of violet–blue luminescence with the precipitates is demonstrated by the local CL spectra as in figure 6, but to determine the exact nature of the luminescent compounds a correlation with electronic structure data would be necessary. Different Er–Si compounds can form during the implantation and annealing treatments. However, XRD results indicate Er_5Si_3 as the possible main compound. The formation of erbium silicides, in particular Er_3Si_5, has been reported [20] in epitaxial Er-doped silicon.

In the case of the samples implanted only with erbium, the high-temperature annealing produces the broad luminescence band shown in figure 3. Weak emission in the blue range was observed in the Er-deposited samples of [16]. In this work the blue emission, which extends into the green range, appears as the only visible band of the spectrum. We suggest that this band arises by activation of the erbium-implanted ions and contains the green luminescence related to intra-ionic Er^{3+} transitions as well as a blue component. Blue luminescence associated with activated erbium ions has been reported for GaN samples implanted with Er and annealed in nitrogen at 1000 °C, which is similar to the treatments used in this work.

4. Conclusions

In conclusion, erbium and oxygen co-implanted amorphous silicon show different visible CL bands appearing after thermal treatments in nitrogen. The presence of oxygen ions enhances the luminescence in the green–red range which is related to erbium oxide. Annealing causes the formation of Er–Si complexes or precipitates which have been found to produce intense luminescence in the violet–blue range with a band peaked at about 330–340 nm.

Acknowledgments

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