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Abstract
Visible luminescence from erbium oxide layers grown on crystalline and amorphous silicon (c-Si and a-Si) has been investigated. The results show strong red and green cathodoluminescence bands due to intraionic Er^{3+} radiative transitions at room temperature. The use of c-Si or a-Si as substrate led to a red or green dominant emission, respectively, which has been explained in terms of the oxygen content in the substrate. The results obtained from samples grown in different atmospheres also support this assumption.

1. Introduction

The possibility of achieving silicon-based optoelectronic devices, which is related to efforts to develop efficient light emitting silicon, has attracted much attention in the last decade since it allows the device integration in the available silicon (Si) technology. It is well known that Si is not a suitable semiconductor for optical purposes due to its indirect gap and low quantum efficiency. To overcome these drawbacks, the incorporation of rare earth elements to a Si matrix, in particular erbium (Er) ions, emerges as one promising method to obtain luminescent material, because of the high Er^{3+} intraionic 4f emission [1, 2]. Many attempts have been made to incorporate Er in different Si substrates, i.e. crystalline [3–5], amorphous [6–8] and/or porous Si [9]. Due to the low diffusivity of Er in Si, Er implantation appears as the most common way to dope Si with Er efficiently [10,11]. However, the luminescence efficiency achieved is still rather low and in general restricted to low temperature. Alternatively, Suezawa *et al* [12] proposed different doping methods and showed that only annealing n-type Czochralski Si in Er vapour at high temperatures (1150°C) led to a strong infrared photoluminescence (PL) emission related to an erbium oxide (Er_2O_3) overlayer on Si [12]. On the other hand, it has been generally accepted that the presence of oxygen in Si substrates enhances the efficiency of Er emission [10,12].

The Er^{3+} ion also exhibits efficient visible luminescence generated by infrared excitation through up-conversion processes [13]. Luminescence in the visible range produced by Er doping of different semiconductor materials has been reported, e.g. GaN [14–16] and oxides, e.g. SiO_2 [17] and ZnO–TeO_2 [18]. The results obtained until now indicate that the light emission both in the visible and in the infrared range is not much influenced by the host lattice.

In this paper, we report strong visible cathodoluminescence (CL), even at room temperature, after Er deposition on Si followed by thermal treatment. Crystalline and amorphous Si (c-Si and a-Si) were used as substrates and the thermal treatments were performed in oxygen or nitrogen atmospheres. The CL spectra exhibit three visible bands in the blue, green and red ranges, whose relative intensities depend on the sample and the annealing temperature. The luminescence of Er_2O_3 powder used as reference sample was also investigated.

2. Experimental set-up

Samples labelled c-Si/Er/O were obtained by vapour deposition of Er on a c-Si wafer followed by annealing

at 950°C for 1 h in oxygen atmosphere. In other set of samples, Er deposition was carried out on a-Si and the annealing at 950°C for 1 h was carried out either in oxygen or nitrogen atmosphere. These samples were labelled a-Si/Er/O and a-Si/Er/N, respectively. a-Si films with a thickness of about 2 μm were obtained by low-pressure chemical vapour deposition on Si at 570°C and a pressure of 0.4 torr. The Er_2O_3 powder with a purity of 99.9% was provided by Sigma-Aldrich.

The samples were investigated by the CL mode of operation in a Hitachi S2500 SEM, in the temperature range of 80–300 K. For the detection of visible light a Hamamatsu R-928 photomultiplier was used, while for the near infrared light a cooled ADC Ge detector was employed [19]. The PL measurements were performed with a CD 900-spectrometer system from Edinburgh Instruments. The samples were cooled at 10 K in a closed-cycle helium cryostat. The excitation sources were a He–Cd laser of 325 and 442 nm with an excitation power of 50 mW, and an Ar–ion laser (lines 514.5, 488 and 457.9 nm) with an excitation power of 20 mW. X-ray diffraction measurements were carried out to check Er incorporation into Si. In order to study Er distribution, mapping of this element was carried out by x-ray wavelength dispersive spectrometry (WDS) in a JEOL JXA-8900 M superprobe.

3. Results and discussion

Typical secondary electron images of the different samples used in this work are shown in figure 1, corresponding to c-Si/Er/O (figure 1(*a*)), a-Si/Er/O (figure 1(*b*)) and a-Si/Er/N (figure 1(*c*)). The nitrogen treated a-Si presents a more uniform surface than the oxygen treated one. The crystalline substrate led to a film with the presence of cracks related to hillocks (figure 1(*a*)). X-ray diffraction microanalysis has confirmed the presence of Er_2O_3 in all the samples. The CL images of the samples were featureless, showing a very homogeneous emission all over the surface.

The CL spectra at 90 and 300 K of the c-Si/Er/O sample are shown in figures 2(*a*) and (*b*), respectively. Three set of peaks are observed: (a) a weak blue band with two peaks at 375 and 410 nm, respectively, (b) a sharp, more intense, green band peaked at about 550 nm and (c) a red band composed of two peaks at 655 and 675 nm with moderate intensity. These bands correspond to some of the visible intraionic transitions of Er^{3+} ion in other matrix materials like GaN [15] and zinc-telluride glasses [18]. The CL spectrum of Er_2O_3 powder obtained under the same experimental conditions is also shown in figure 2. The only difference between the c-Si/Er/O spectrum and that of Er_2O_3 appears in the blue region in which a broad emission underlying the 375 and 410 nm peaks is appreciable in the c-Si/Er/O sample and not in the oxide powder. The relative intensities of the CL visible bands depend on the temperature, as figure 2 shows. The green band is dominant at 90 K and decreases as the temperature increases, while the red band shows no changes with temperature and becomes dominant in the CL spectrum at room temperature. These trends are the same for the Er_2O_3 powder and for the c-Si/Er/O sample and have been previously observed [18] in PL measurements of Er-doped zinc-telluride glasses. The CL signal in the
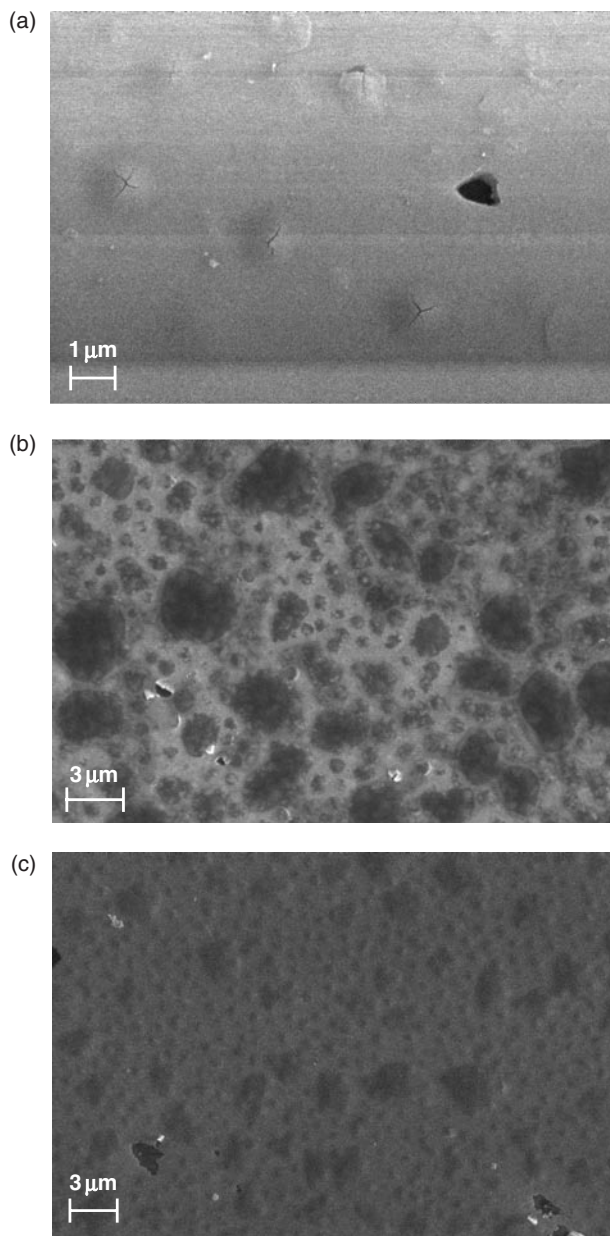
(a)

1 μm

(b)

3 μm

(c)

3 μm

Figure 1. Secondary electron images from (*a*) c-Si/Er/O, (*b*) a-Si/Er/O and (*c*) a-Si/Er/N.

infrared range was too weak to record spectra of the Er treated Si samples but the Er_2O_3 powder showed strong CL emission in the 1.0–1.6 μm range as well as visible emission (figure 3).

In PL spectra (figure 4) neither green nor red emission has been observed even during excitation with different lasers and wavelengths mentioned above. Only a blue broad band, which could be related to the blue background of the CL spectrum, was detected. Differences between PL and CL spectra have been often reported in semiconductor materials. This is attributed to the different excitation energies used in both kinds of experiments and to a more selective character of the PL excitation. These results suggest that the Er-induced luminescence is only slightly influenced by matrix effects and
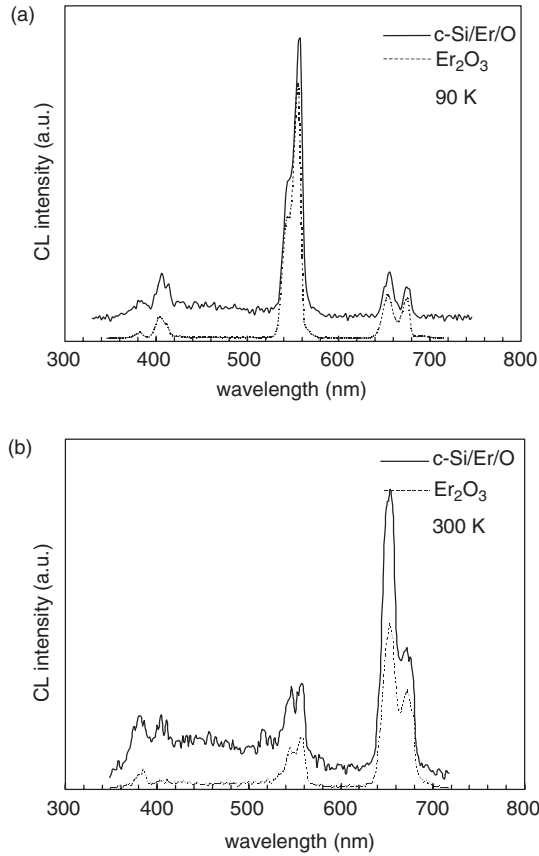
(a)

(b)

Figure 2. CL spectra of c-Si/Er/O sample and Er$_2$O$_3$ powder recorded at (*a*) 90 K and (*b*) 300 K.
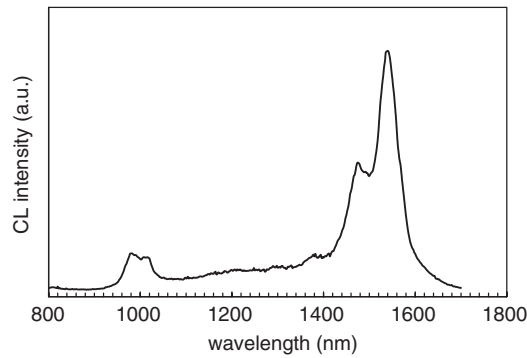

Figure 3. CL spectrum of Er$_2$O$_3$ powder at room temperature in the infrared range.
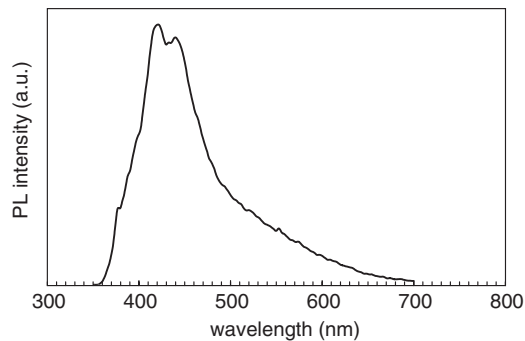

Figure 4. PL spectrum of c-Si/Er/O at 10 K in the visible range. The excitation wavelength was 325 nm.
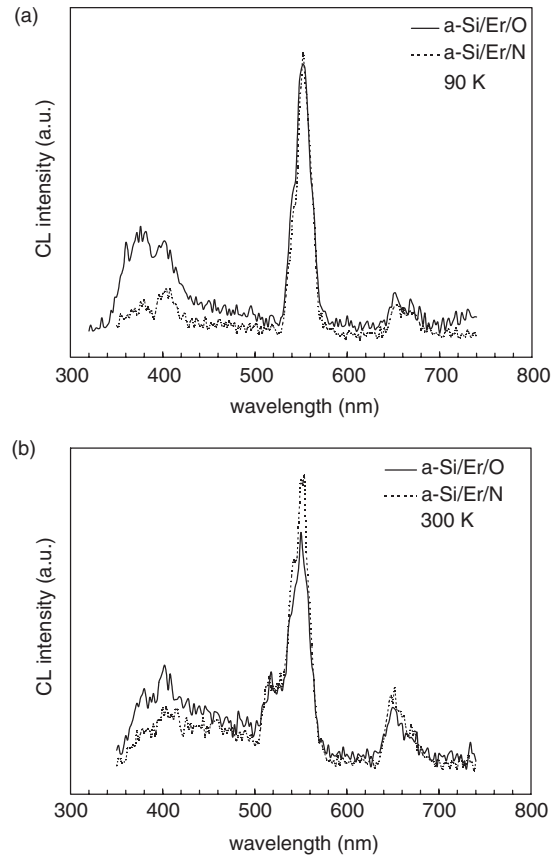
(a)

(b)

Figure 5. CL spectra of a-Si/Er/O and a-Si/Er/N recorded at (*a*) 90 K and (*b*) 300 K.

confirm that the local environment of the Er^{3+} ions in Er-doped Si is similar to the Er^{3+} environment in Er$_2$O$_3$, in agreement with previous Mössbauer spectroscopy studies of amorphous hydrogenated Si [20]. Therefore, the similarities in the visible CL spectra of the c-Si/Er/O and the Er$_2$O$_3$ samples confirm that the interaction of Er with oxygen plays an important role in the luminescence mechanism. The results also show that the excitation mechanisms and the host matrix have a certain influence on the relative intensities of the CL emission bands.

In the case of Er deposited on a-Si, a strong CL emission in the visible region showing blue, green and red bands (figure 5) is observed in the temperature range of 90–300 K. The green band is always the dominant one in the CL spectra in the whole temperature range. The difference between the CL spectra of a-Si/Er/O and a-Si/Er/N samples is apparent in the blue band, which is more intense in the sample treated with oxygen than in the nitrogen treated one. This effect is clearly appreciated in the CL spectra recorded at 90 K as shown in figure 5(*a*). A blue emission has been only previously detected in PL studies of up-conversion processes and attributed to intraionic transitions in Er^{3+} ions [13]. In the PL spectra obtained from c-Si/Er/O samples, the blue band dominates. The present results suggest the possibility of the formation of Er–N complexes besides the Er–O ones which could influence the blue emission. A comparison between the CL spectrum of a c-Si/Er/O sample and a-Si/Er/O one is shown in figure 6. The
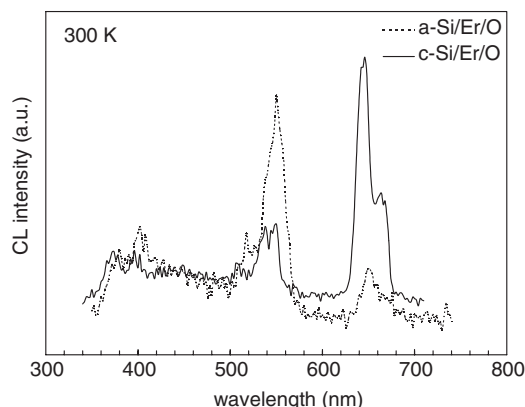
Figure 6. Comparison between the CL spectrum from crystalline and amorphous substrate.

main difference appears in the red band, which is very intense in c-Si but rather weak in a-Si substrate. Jaba [18] reported an increase of the relative intensity of the red band with increasing Er_2O_3 concentration. Since the crystalline substrate grown by the Czochralski method has a higher amount of oxygen than the amorphous layer, this result suggests that the formation of Er_2O_3 is determined by the oxygen content of the substrate rather than by the atmosphere during the thermal treatment. This possibility is supported by the fact that the red band is similar in a-Si/Er/O and a-Si/Er/N samples.

4. Conclusions

Electron excitation in the SEM leads to efficient visible CL related to transitions of Er^{3+} ions in different Si substrates at room temperature. In fact, narrow green and red dominant CL emissions were observed in Er treated a-Si and c-Si, respectively, possibly due to the different oxygen content in the substrate. Hence, CL is an alternative to the previously reported PL with selective excitation at low temperature to excite luminescence in the visible range. The uses of crystalline or amorphous substrate and of oxygen or nitrogen ambient in thermal treatments induce different competition processes between radiative transitions in Er^{3+} ions.

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