Room-temperature luminescence from Er-implanted semi-insulating polycrystalline silicon

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Semi-insulating polycrystalline silicon films with oxygen concentrations in the range 4–27 at. % were deposited by low-pressure chemical vapor deposition of SiH_4 and N_2O onto silicon substrates, annealed at 920 °C, and then implanted with 2×10^{15} 500 keV Er ions/cm^2. After annealing at temperatures in the range 300–900 °C, the samples show intense room-temperature luminescence around 1.54 μm, characteristic of intra-4f emission from Er^{3+}, upon excitation using an Ar ion laser. The luminescence intensity increases with increasing oxygen concentration in the film. The luminescence is attributed to Er^{3+} ions in oxygen-rich shells around Si nanograins, excited by a photocarrier-mediated process.

Efficient light emission from semiconductors compatible with silicon-based technology is important for the integration of optics and electronics. Unfortunately, in silicon the radiative band-to-band recombination efficiency is too small for practical use in optoelectronic devices. An alternative way to achieve light emission from Si is by doping with Er. When incorporated in the trivalent charge state, Er shows intra-4f luminescence around $\lambda = 1.54$ μm, a standard telecommunication wavelength. Several studies have been devoted to the incorporation of Er in Si, and photoluminescence[1–3] and electroluminescence[4] have been observed. Although Er concentrations as high as 10^{20} cm^{-3} can be incorporated in single crystal Si,[5] the Er emission is very inefficient and only very small signals are observed at room temperature.[2,3] Recently, it has been demonstrated that the luminescence of Er-doped silicon is enhanced by the presence of low concentrations of oxygen[2,6] through the formation of Er-O complexes[7] in which Er has the trivalent charge state. In order to fully activate the high Er concentrations needed for practical use, oxygen concentrations in excess of 1 at. % are necessary.[8]

Semi-insulating polycrystalline silicon (SIPOS) is a material which contains large concentrations of oxygen, but still shows semiconducting properties. The microstructure of the material after annealing above 800 °C consists of silicon nanograins surrounded by oxygen-rich SiO_x shells. Conductivity measurements as a function of temperature[9] demonstrate the semiconducting nature of the material, which has resistivities ranging from 10^6–10^9 Ω cm at room temperature. SIPOS is used in silicon-integrated circuit technology as a passivation layer. The combination of its high oxygen content and semiconducting properties also makes SIPOS a very interesting candidate as host material for Er. As will be shown in this letter, SIPOS films doped with Er by ion implantation show intense 1.5 μm luminescence at 300 K. This is the first observation of room-temperature light emission from a Si-based semiconductor.

The ≈ 1-μm-thick SIPOS layers were deposited onto single crystal (100) Si substrates by low-pressure chemical vapor deposition of SiH_4 and N_2O at a substrate temperature of 620 °C. Changing the SiH_4/N_2O flow ratio resulted in layers with different oxygen contents, ranging from 4 to 27 at. %. After deposition, the wafers were annealed at 920 °C for 30 min in an O_2 atmosphere. The composition of the films was measured by 2.0 MeV ^{4}He Rutherford backscattering spectrometry (RBS). The SIPOS films were then implanted with 500 keV Er ions to a fluence of 2×10^{15} ions/cm^2, with the samples held at room temperature. Reference samples of (100) n-type Czochralski-grown Si (1–4 Ω cm) as well as 0.45 μm thick thermally grown SiO_2 on (100) Si were implanted in the same batch. The implantation resulted in a Gaussian implantation profile peaked at ≈ 150 nm depth with a full width at half-maximum of ≈ 100 nm, as measured by RBS. The Er peak concentration was ≈ 0.4 at. %. The samples were subsequently annealed in vacuum ($\approx 4 \times 10^{-7}$ mbar) for 30 min at temperatures ranging from 300 to 1100 °C. The annealing did not cause any measurable diffusion of the Er. Luminescence spectroscopy measurements were performed by illuminating the samples with one of the lines of an Ar ion laser at pump powers ranging from 50 to 750 mW. The laser light was chopped at a frequency of 13 Hz. The luminescence signal was analyzed by a single-grating monochromator at a resolution of 6 nm, detected using a liquid-nitrogen cooled Ge detector and recorded with a lock-in amplifier.

Figure 1 shows the room-temperature luminescence spectra of Er-implanted pure Si, SiO_2, and SIPOS containing 4, 11, and 27 at. % oxygen, after annealing at 500 °C for 30 min. The implanted pure Si sample shows no detectable Er-related luminescence. The SiO_2 sample shows the characteristic spectrum of Er^{3+} in silica, peaked at $\lambda = 1.54$ μm.[10] In SIPOS, the same well-defined structured peak is observed around $\lambda = 1.54$ μm, and is also attributed to intra-4f transitions in Er^{3+}. The Er luminescence intensity in SIPOS increases with oxygen content; at an oxygen con-

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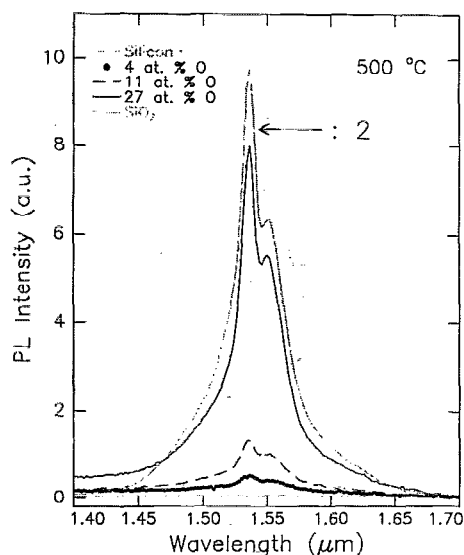[a] Permanent address: Dipartimento di Fisica della Universitá, Corso Italia 57, I 95129, Catania, Italy.

FIG. 1. Room-temperature luminescence spectra of Si, SiO_2, and SIPOS containing 4, 11, and 27 at. % O implanted with 2×10^{15} 500 keV Er/cm^2. The silicon signal almost coincides with the horizontal axis. The samples were annealed at 500 °C for 30 min in vacuum. The 514.5 nm line of an Ar ion laser was used as a pump source at 750 mW. The spectral resolution was 6 nm.

FIG. 3. Room-temperature luminescence peak intensity at $\lambda = 1.535$ μm vs pump wavelength for Er-implanted SIPOS containing 27 at. % oxygen annealed at 500 °C (closed circles) and 900 °C (closed triangles). For comparison the spectrum of Er-implanted SiO_2 annealed at 900 °C is also reported. The pump power was 125 mW for each wavelength.

tent of 27% the peak intensity is half that of the Er-doped SiO_2 film.

The behavior of the luminescence peak intensity upon annealing for Er-implanted SIPOS containing 27 at. % O is shown in Fig. 2. The intensity in the as-implanted sample is almost zero. The intensity increases upon annealing up to 500 °C, is approximately constant up to 700 °C, and levels off above 800 °C. Measurements on samples implanted with 1×10^{15} Er/cm^2 (not shown) show that after 1100 °C annealing the luminescence intensity decreases strongly.

Figure 3 shows the luminescence excitation spectra taken by monitoring the luminescence peak intensity at 1.535 μm at 6 different pump wavelengths ranging from 457.9 to 514.5 nm, at a constant pump power of 125 mW. This wavelength scan was performed on Er-implanted
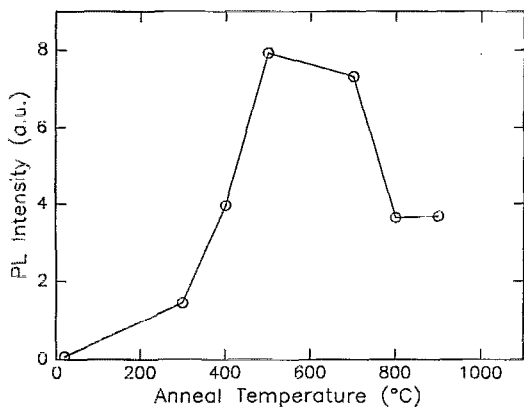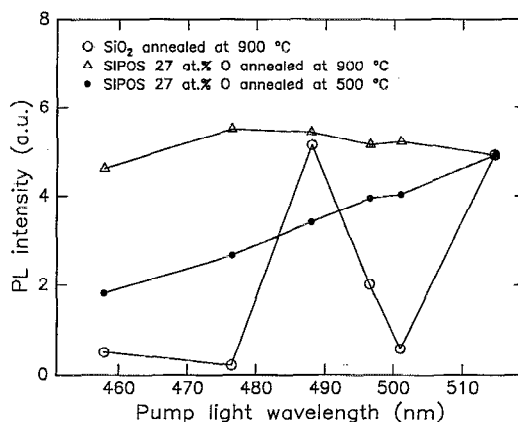
SIPOS containing 27 at. % annealed at 500 °C (closed circles) and at 900 °C (open triangles), as well as on the Er-implanted SiO_2 film (open circles). The signals are normalized to the intensity at 514.5 nm in order to compare the trends in the different materials. For SiO_2, strong variations in intensity as a function of pump wavelength are observed. These variations reflect the peaked structure of the absorption bands in Er^{3+};[11] the peaks at 488 and 514.5 nm correspond to the $^4I_{15/2} \rightarrow {}^4F_{7/2}$ and to the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transitions in Er^{3+}, respectively. In contrast, the excitation curves for SIPOS do not show any structured feature. An almost constant signal as a function of wavelength is observed for the SIPOS film annealed at 900 °C, while a monotonic increase with pump wavelength is measured for the sample annealed at 500 °C.

Several conclusions can be drawn from the data in Figs. 1–3, concerning the local environment around the Er^{3+} in SIPOS and its excitation mechanism. First of all, the absence of structure in the excitation spectra for Er-doped SIPOS (Fig. 3) indicates that the excitation of Er does not result from direct absorption. Instead, the results suggest that the Er^{3+} ions are excited through a photocarrier-mediated process.

Second, the luminescence spectra shown in Fig. 1 for Er-doped SIPOS and SiO_2 are quite similar in shape, indicating that the local environment of the luminescent Er ions is O-rich. Moreover, the peak intensity of the spectra increases with the oxygen fraction in the SIPOS layer. These results suggest that the observed luminescence originates from Er^{3+} in the SiO_x shells around the Si nanocrystals. This raises the interesting speculation that photocarriers generated in the Si grains would transfer energy to the Er in the SiO_x shells. Note that the typical silicon grain size in the SIPOS films is only about 5 nm at 27 at. % O and the surrounding oxide about 1–2 nm thick.[9–12] As it has been shown in oxide materials, energy exchange mechanisms (such as Er-Er interaction) can indeed take place over several interatomic distances.[13]

The behavior of the luminescence peak intensity as a

FIG. 2. Room-temperature luminescence peak intensity at $\lambda = 1.535$ μm vs annealing temperature for SIPOS containing 27 at. % oxygen and implanted with 2×10^{15} 500 keV Er/cm^2. The anneals were performed for 30 min in vacuum. The 514.5 nm of an Ar ion laser was used as pump source.

function of annealing temperature reported in Fig. 2 can be related to microstructural changes in SIPOS during annealing. The room-temperature Er implant causes amorphization of the Si nanocrystals. As determined by transmission electron microscopy[14] annealing up to 500 °C leaves the material amorphous. The observed initial increase in luminescence intensity may be explained by four effects. Annealing causes (1) a reduction in the number of implantation-induced defects which quench the luminescence, as well as (2) an increase in the number of optically active Er ions, i.e., Er ions finding a sixfold oxygen coordinated site. Furthermore, (3) annealing causes structural relaxation and defect annealing, increasing the carrier lifetime in the amorphized film,[15] which enhances the excitation efficiency. Last, (4) in as-implanted amorphous Si the absorption coefficient of the pump light is very high,[16] implying that most of the pump light is absorbed close to the surface and cannot reach the Er-implanted region. Annealing at 500 °C decreases the absorption coefficient,[16] leading to better overlap between the Er implant profile and the absorbed light. This leads to an increase of the carrier density in the vicinity of the Er ions, thus increasing the luminescence.

Annealing at temperatures above 800 °C causes recrystallization of the Si nanocrystals,[9,14] the absorption coefficient of pump light decreases from roughly 2×10^5 cm^{-1} in amorphous Si to 10^4 cm^{-1} in the crystal phase.[16] This implies less pump light is absorbed in the Er-implanted region after crystallization, and so less carriers are available for excitation of Er^{3+}, leading to a decrease in the luminescence. The strong decrease in intensity upon annealing at 1100 °C is attributed to Er precipitation in the SiO$_x$ phase, as reported earlier for Er-implanted silica,[10] or a breakup of the nanograin/oxide shell structure.

The observed trends for the Er-luminescence in SIPOS as a function of pump wavelength shown in Fig. 3, may also be explained in terms of the absorption depth of the pump light. For the 500 °C annealed (amorphous) sample the absorption depth is estimated to be on the order of 50 nm, i.e., somewhat shallower than the Er-implanted region. An increase in pump wavelength leads to a decrease in absorption coefficient for amorphous Si,[16] and therefore a larger absorption depth. This, in turn, leads to a more efficient overlap between Er profile and pump light. This explains the increase with pump wavelength shown in Fig. 3. For the 900 °C annealed (recrystallized) sample the pump absorption depth is much larger than the depth of the Er profile. Thus, changes in absorption with pump wavelength will not strongly influence the overlap between the Er implantation profile and the pump. This leads to the constant luminescence signal for the 900 °C annealed SIPOS sample in Fig. 3.

In conclusion, we report the first demonstration of room-temperature light emission from an Er-implanted silicon-based semiconductor. The material, known as semi-insulating polycrystalline silicon, contains oxygen concentrations between 4 and 27 at. % and was implanted with 2×10^{15} Er/cm^2. When optically pumped at ~ 500 nm, intense Er-related luminescence around 1.5 μm is observed. The Er luminescence depends strongly on the SIPOS microstructure, and is attributed to Er^{3+} in SiO$_x$ shells around Si nanograins. It is suggested that the Er^{3+} is excited by a process mediated by carriers generated in the Si grains. The semiconducting nature of SIPOS, combined with the observation that Er in SIPOS can be electrically excited, implies that Er-doped SIPOS has a strong potential as material for electrically activated light emission in silicon-based optoelectronics.

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