

Room Temperature Photoluminescence of Er-Doped Porous Silicon at 1.54 μ m

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Porous silicon layers of $\sim 10 \mu\text{m}$ thickness are uniformly doped with Er ions at a density more than $10^{19}/\text{cm}^3$ by an electro-chemical method and an intense photoluminescence at 1.54 μm due to intra-4f-shell transition of Er ions is observed at room temperature. The 1.54 μm luminescence intensity is related with the peak photoluminescence wavelength of the starting porous silicon layers and becomes maximum at 0.8 μm . This result suggests that the electron-hole recombination energy of porous silicon layers excite the 4f shell electrons from the ground ($^4I_{15/2}$) to the third excited ($^4I_{9/2}$) states. This is the reason for the small thermal quenching and the intense room temperature luminescence at 1.54 μm .

1. INTRODUCTION

Rare-earth (RE) doped semiconductors are known to show sharp and thermally stable luminescence¹⁾. Among various combinations of RE ions and host semiconductors, Er-doped silicon is very attractive, since it illuminates at 1.54 μm due to Er intra-4f-shell transition from $^4I_{13/2}$ (first excited state) to $^4I_{15/2}$ (ground state) and may be used for silicon based optoelectronic devices²⁾. The main problem of Er-doped silicon is its low emission efficiency at room temperature due to large thermal quenching. It is also difficult to incorporate high density of Er ions ($> 10^{19}/\text{cm}^3$) deep into silicon to attain a sufficient luminescence intensity.

It has been shown that the thermal quenching is reduced by using wide-gap host semiconductors³⁾. It has also been shown that the incorporation of oxygen increases significantly the emission intensity of Er-related luminescence at 1.54 μm ⁴⁻⁶⁾.

We have developed a electro-chemical method for incorporating Er ions into porous silicon layers (PSLs). Er ions are incorporated almost uniformly into pores of PSLs and by annealing in the Ar/O₂ atmosphere, Er ions are taken into nanostructure crystalline silicon and are oxidized at the same time. The obtained Er-doped PSLs show a strong illumination at 1.54 μm at room temperature.

2. EXPERIMENTAL

Porous silicon layers (PSLs) are formed by anodic etching of Czochralski-grown p-type Si (100) (several $\Omega\text{-cm}$) substrate surfaces in a 46% HF/H₂O solution. After rinsed with pure water, PSLs are immersed in ErCl₃/ethanol solution and are negatively biased relative to a counter platinum electrode to draw Er³⁺ ions inside pores of PSLs by the electric field. After

the Er incorporation process, samples are annealed at high temperatures (900 - 1300°C) for 30 sec in a 20% O₂/Ar atmosphere using a lamp furnace. PL measurements are performed by illuminating samples with Ar laser light (514.5 nm). The luminescence signal is monitored using a single-grating monochromator (Jobin-Yvon HR320) and a cooled germanium pin photodiode.

3. RESULTS AND DISCUSSION

Fig.1 shows secondary ion mass spectrometry (SIMS) depth profiles of Er and C atoms in a PSL. The thickness of this PSL is about 11 μm measured from the scanning electron micro scope (SEM) observation. It is shown that Er atoms are incorporated almost uniformly over the entire PSL at $6-7 \times 10^{19}/\text{cm}^3$.

The total amount of Er ions incorporated into the PSL corresponds to about 1/10 of the total charge flow to the PSL during the Er-doping process (assuming Er³⁺ ions). C atoms are found to be incorporated over the PSL at more than one order of magnitude higher densities than Er atoms and the most of the charge flow is ascribed to C-related ions.

Fig.2 shows the change in the photoluminescence (PL) spectra of Er-doped PSLs against annealing temperature. The Er-related 1.54 μm luminescence begins to grow above 1240 °C. As shown in the insert, the luminescence from the PSL is observed after this high temperature annealing, though the spectrum is slightly changed. Note that neither the 1.54 μm luminescence nor the luminescence from PSLs is observed when the samples are annealed in a pure Ar atmosphere.

Fig.3 shows the temperature dependence of the 1.54 μm luminescence. Different from Er-doped pure Si crystal which shows a strong thermal quenching above $\sim 100\text{K}$, our Er-doped PSLs show very small thermal quenching and strong luminescence at room temperature.

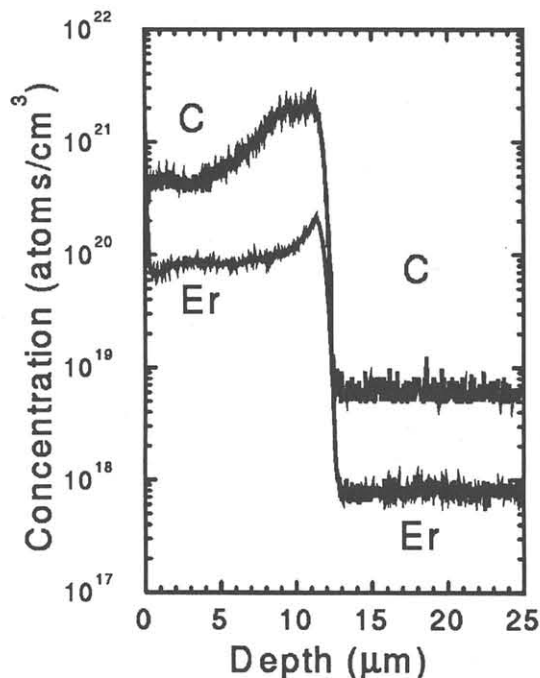


Fig.1: SIMS depth profiles of Er and C atoms in an electrochemically Er-doped PSL.

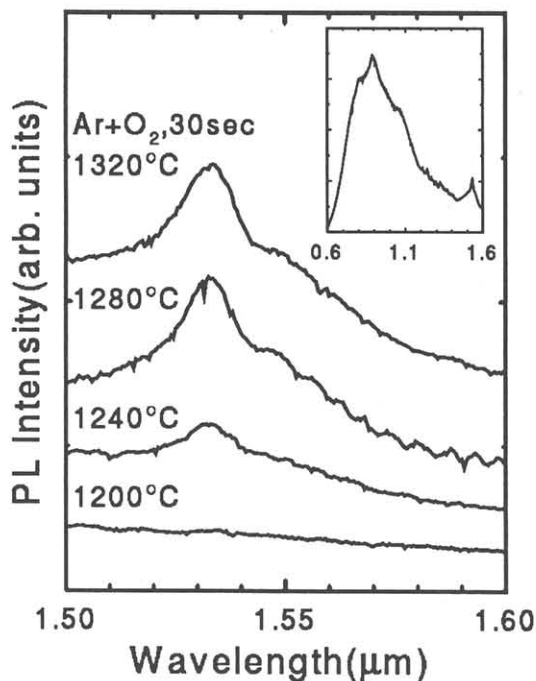


Fig.2: Change in the photoluminescence spectra around $1.54 \mu\text{m}$ of an Er-doped PSL with increasing annealing temperature in Ar/O_2 atmosphere.

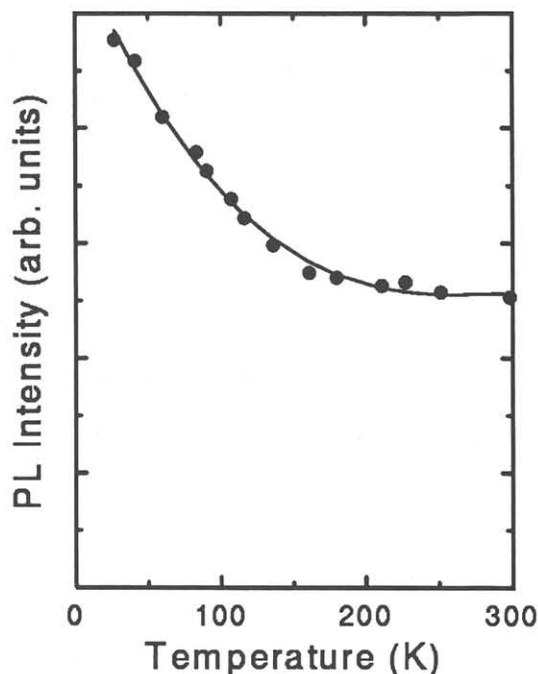


Fig.3: Temperature dependence of the Er-related $1.54 \mu\text{m}$ luminescence.

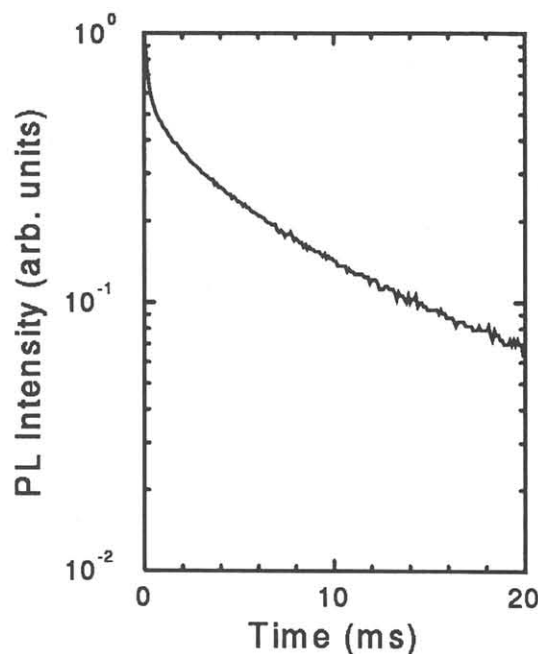


Fig.4: Fluorescence decay of the Er-related $1.54 \mu\text{m}$ luminescence at room temperature.

Fig.4 shows the fluorescence decay of the $1.54 \mu\text{m}$ at room temperature. A fast initial decay with an exponential decay time of $0.8 \sim 1 \text{ ms}$ is followed by the main decay with the decay time of about 13 ms . The latter decay time is comparable to Er ions in semiconductors at low temperatures where no thermal quenching is observed.

The interesting and important results related with the excitation mechanism is the dependence of the $1.54 \mu\text{m}$ luminescence intensity on the PL spectrum of the starting PSLs. PSLs of different PL spectra are

prepared by changing the anodic conditions, and then the same Er-doping and annealing processes are given to them. Fig. 5 shows the intensity of the $1.54\ \mu\text{m}$ luminescence against the peak energy of the starting PSLs. In the insert are shown the PL spectra of the starting PSLs. The intensity of the $1.54\ \mu\text{m}$ luminescence becomes maximum at the PSL peak wavelength of $\sim 0.8\ \mu\text{m}$ and decreases rapidly on both sides. This result clearly indicates that 1) Er ions are excited by energy transfer from PSLs and not directly with Ar laser light and that 2) Er intra-4f shell is excited from the ground state $^4I_{15/2}$ to possibly the third excited state $^4I_{9/2}$ as shown in Fig.6. With this three-level excitation and relaxation system, the energy backflow from Er ions to host PSLs is suppressed. This may be the reason for the small thermal quenching of the Er-related $1.54\ \mu\text{m}$ luminescence.

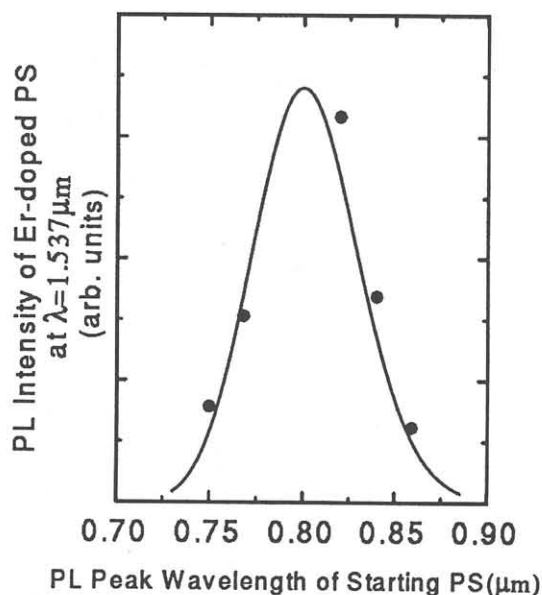


Fig.5: The $1.54\ \mu\text{m}$ Er-related emission versus peak PL energy of the starting PSLs.

In conclusion, Er ions are easily incorporated deep into PSLs at more than $10^{19}/\text{cm}^3$ by electro-chemical method. Intense room luminescence at $1.54\ \mu\text{m}$ is obtained after annealing at $1300\ ^\circ\text{C}$ in an oxygen containing atmosphere. By adjusting the PL spectrum of the starting host PSL, effective excitation of Er ions with small thermal quenching is obtained. This method may be useful to form Si-based optoelectronic devices.

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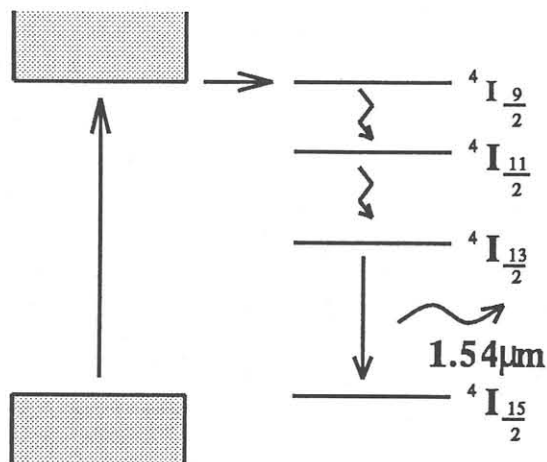


Fig.6: Three-level excitation and relaxation of Er-doped porous silicon layers with a peak wavelength at $\sim 0.8\ \mu\text{m}$.

4. REFERENCES

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