PHOTOLUMINESCENCE OF ERBIUM IN AMORPHOUS SILICON: STRUCTURAL RELAXATION AND OPTICAL DOPING

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ABSTRACT

Photoluminescence of erbium in ion-implanted amorphous Si has been observed after annealing at 400°C. In addition, a broad band of luminescence attributed to intrinsic defects in amorphous Si is present. The background level steadily increases with increasing anneal temperature. The fluorescence lifetimes of either the Er or the background in all samples are $\leq 150\,\mu$sec.

INTRODUCTION

Recently there has been substantial interest in Er in crystal Si (c-Si) because of the possibility of realizing optoelectronic devices [1-4]. Erbium in c-Si, as in many other hosts, displays intra-$4f$ luminescence near $1.5\,\mu$m. However, the solubility of Er in c-Si is only $\approx 1 \times 10^{18}\,/\mathrm{cm}^3$, which severely constrains potential optoelectronic applications [5,6]. Attempts to optically activate higher Er concentrations in c-Si by thermal annealing results in defect and silicide formation [5]. To introduce Er in c-Si by ion implantation, most workers avoid forming an amorphous Si (a-Si) layer by implanting at elevated temperatures [5,7]. This is because recrystallizing an Er-doped a-Si layer results in defected epitaxy or polycrystal Si formation, in addition to anomolous Er redistribution [5,8].

The difficulties in doping *crystal* Si with Er might be avoided by using *amorphous* Si instead. Then, the Er concentration can be made arbitrarily high by ion implantation. Recently, photoluminescence (PL) from Er in sputter deposited hydrogenated a-Si has been reported [9], demonstrating that a-Si is a potential host material. Moreover, a-Si layers made by ion implantation are attractive because of the potential for on-wafer optical integration utilizing the higher index of refraction of a-Si relative to c-Si to form waveguides. The major problem, however, is making the Er optically active and pumping it efficiently. In oxide glasses, anneals of up to 900°C are sometimes required to obtain optimal Er luminescence with lifetimes of up to 15 ms [10]. Thermally processing pure a-Si at these temperatures will result in either solid phase epitaxy or polycrystalline nucleation [11]. Furthermore, metals in a-Si often substantially increase the nucleation rate [12], and Er silicide formation could also be a problem [13]. Therefore, only low temperature anneals can be considered to activate Er in a-Si.

By now it is well established that the physical properties of ion implanted a-Si change with low temperature ($\leq$ 500°C) annealing [14]. This has been probed using, for example, infrared or Raman spectroscopy [15,16], calorimetry [17,18], and carrier lifetime measurements [19]. Such changes in properties during annealing are called "structural relaxation," and involve a continuous evolution of the system to lower free energies [14]. Amorphous Si is generally considered to be a continuous random network with the Si atoms being fourfold covalently bound [20], and the observed physical changes are caused by either relaxation of the entire network or point defect annhiliation [14,21,22]. Thermal anneals are thought to optically activate Er in glasses by not only altering the local configuration around the Er, but also by removing the implant damage which enhances non-radiative recombination, resulting in a higher fluorescence lifetime [10]. Structural relaxation of a-Si involves just such configurational changes and defect annihilation. Therefore, it may be possible to optically activate Er in a-Si using only low temperature anneals.

Photoluminescence has been used previously to investigate hydrogenated a-Si [23-25]. Here, the luminescence occurs by recombination of electrons and holes through defect states in the forbidden gap or the band tails. Electron irradiation of a-Si:H creates defect states, causing luminescence which is generally analogous to the defect luminescence observed in irradiated c-Si

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[26,27]. While low concentrations of defects luminesce, higher concentrations quench the luminescence, probably by increasing non-radiative carrier relaxation paths. However, no experiments on photoluminescence as a function of the state of structural relaxation have been reported.

In this paper we will show that implanted a-Si exhibits PL in the infrared. Furthermore, PL from Er is also observed near 1.54 μm. The amount of PL increases with anneal temperature up to 500°C, with Er-doped a-Si showing more PL than intrinsic a-Si. The luminescence lifetimes of both the intrinsic and Er PL are $\leq$ 150 μsec. The low optical activation and short luminescence lifetimes of Er in ion-implanted a-Si suggest that pure a-Si is an unlikely host for optical applications.

EXPERIMENTAL

Amorphous Si layers were made by implanting 3×10^{15} /cm^2 350 keV Si into (100) Si with the substrates held at liquid nitrogen temperature. This generates an a-Si layer $\approx$ 550 nm thick as measured by Rutherford Backscattering Spectroscopy (RBS) in the channeling configuration. Erbium was then implanted at 250 keV to a dose of 5.4×10^{15} /cm^2. At this energy, Er has a projected range of 100 nm and straggling of 50 nm, as measured by RBS. The Er peak concentration is 1.4 at.%, and the profile is completely contained in the a-Si layer. Thermal anneals were performed in vacuum ($\leq 1 \times 10^{-7}$ Torr) for 1 hour at various temperatures up to 500°C.

The samples were mounted in a vacuum chamber on a liquid nitrogen cooled sample holder. Luminescence was excited by pumping optically with an Ar ion laser (200mW, λ = 514.5 nm) chopped at 15 Hz. The luminescence was measured using a monochromator equipped with a liquid nitrogen cooled Ge photodetector. The signal from the detector was fed into a lock-in amplifier using the chopper frequency as a reference. The wavelength of the monochromator was scanned, with the lockin signal and the monochromator wavelength recorded by computer. The spectra presented are not corrected for the detector response, which cuts off near 1.7 μm on the high wavelength side. Optical lifetime measurements were performed using short 1 W Ar laser pulses, with the detector output amplified in the lock-in preamplifier and then displayed on a digitizing oscilloscope. The digitized signal was then averaged for 100 shots to reduce the noise.

RESULTS

No photoluminescence is observed in as-implanted samples; annealing at 200°C for 1 hour is required to observe any signal. Figure 1(a) shows PL spectra for pure a-Si after anneals at 200, 300, 400, and 500°C. The spectra have been offset from each other for clarity. The relative size of the signals indicates the relative amount of PL from each sample. This pure a-Si luminescence covers a broad band from $\sim$ 1.2 μm to 1.7 μm, with the high wavelength side limited by the detector response. With increasing anneal temperature the luminescence signal steadily increases.

Figure 1(b) shows PL spectra of Er-doped a-Si. The anneal temperatures and the relative signal heights are the same as for Fig. 1(a) to facilitate comparison. The spectra of pure and Er-doped a-Si at 200°C are essentially the same. After annealing at 300°C, the Er sample exhibits a much higher PL level than the intrinsic a-Si, but the characteristic 1.5 μm Er line is not visible. A 400°C anneal increases the background further, and Er PL is visible. Figure 2 shows a high resolution PL spectrum taken around the Er signal. It clearly shows a main peak at 1.54 μm with a side peak at slightly higher wavelength, similar to what is observed in glass [10]. Finally, annealing the Er-doped sample at 500°C reduces the background, while some Er PL is still visible. However, transmission electron microscopy indicates that the layer material is still amorphous, although small precipitates cannot be ruled out.

We attempted to determine the photoluminescence lifetimes in pure and Er-doped a-Si annealed at 400 and 500°C, both on the Er peak and on the background. In all samples, the measured decay times were limited by the detector response, yielding an upper limit for the lifetime of $\leq$ 150 μsec. This decay time is some two orders of magnitude shorter than obtained for Er in optical glasses [10], and also faster than in c-Si [28].

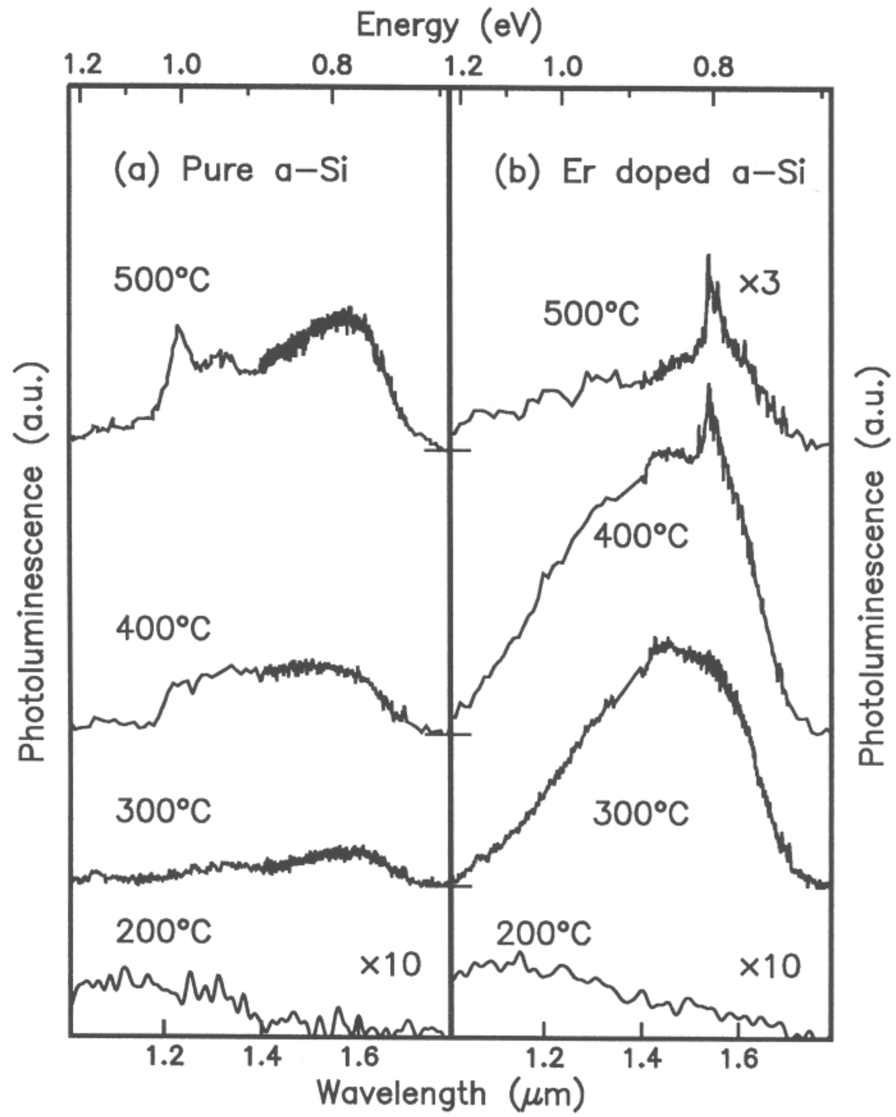

FIG 1. Photoluminescence spectra for (a) pure a-Si and (b) Er-doped a-Si after annealing at 200, 300, 400, and 500°C. Both (a) and (b) are plotted with the same scales, so relative heights are comparable.

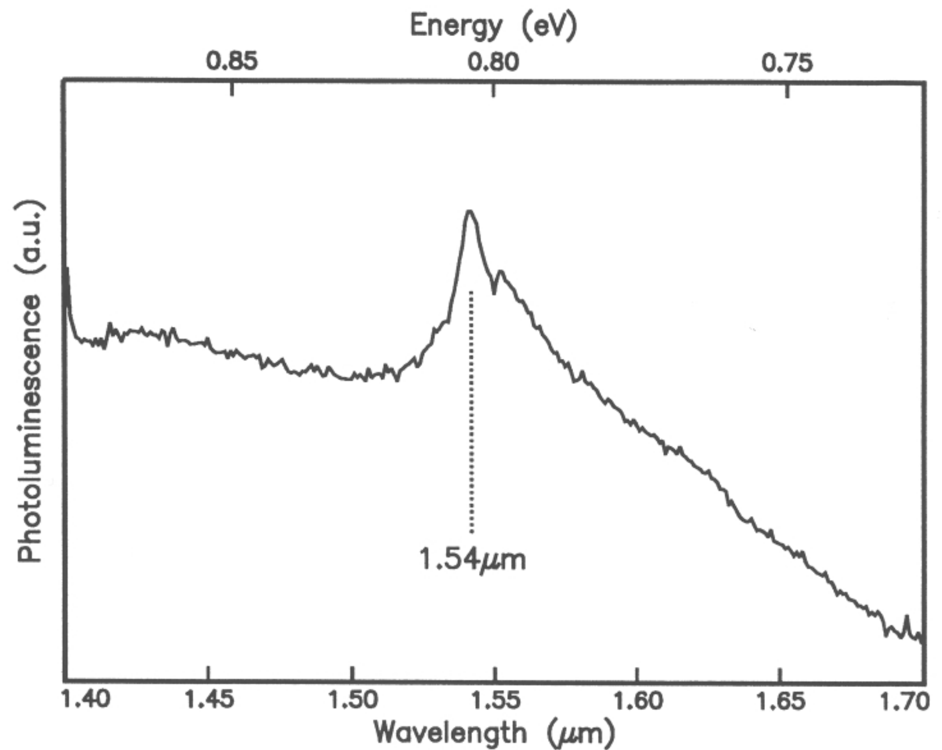

FIG 2. Photoluminescence spectrum from 400°C annealed Er-doped a-Si. The Er signal is clearly visible as two peaks on the intrinsic a-Si background. The main peak is centered on $\lambda = 1.54\,\mu m$.

DISCUSSION

Pure ion-implanted a-Si annealed at or above 200°C exhibits photoluminescence in a broad band in the infrared, and the amount of PL increases with anneal temperature. Similar luminescence is observed in hydrogenated a-Si, and has been attributed to defect energy levels in the a-Si band gap [23]. It is then initially surprising that the PL signal would increase with annealing because structural relaxation is believed to reduce the number of structural and electrical defects. For example, the carrier lifetime increases by an order of magnitude upon annealing at 500°C [19]. However, in photoluminescence not only are the number of defects important, but so is the ratio between radiative and non-radiative lifetimes. As has been demonstrated in a-Si:H, a large number of defects quenches the PL [26]. Similarly, ion irradiation in silica glass reduces the PL signal [29]. Thus, the increase in the a-Si PL can be caused by a decrease in the non-radiative recombination rate, i.e. defect annealing accompanying structural relaxation. A second possible reason for the increase in a-Si PL with anneal temperature is that the absorption coefficient is reduced by annealing [30], so the a-Si volume excited by the Ar laser increases with anneal temperature. Since the carrier lifetimes in pure a-Si are very short [19], ruling out substantial carrier diffusion, essentially only the excited volume contributes to the PL signal.

Annealing Er-doped a-Si at 400°C leads to a PL signal near $1.54\,\mu m$. The structure of the Er peak is similar to what has been observed in a-Si:H and other amorphous materials [9,10]. The Er signal in these samples is on top of the large a-Si background. In contrast, for a-Si:H very little background is observed at these wavelengths; instead band-edge luminescence near $1\,\mu m$ is the dominant a-Si contribution. However, H is introduced in a-Si to passivate defects to improve the electrical properties of the material. In our un-hydrogenated a-Si there is no passivation, and

the defect luminescence is much stronger than in a-Si:H.

The strong absorption of the 514.5 nm wavelength used to pump the a-Si may also explain the small Er signal observed in the 400°C annealed sample. In c-Si, the dominant pumping mechanism for Er is through electron–hole pairs generated by the laser [4]. Because of the short carrier lifetime in a-Si [19], only pairs generated in the immediate vicinity of the Er can transfer energy. A PL spectra of the 400°C annealed Er sample using the 488 nm Ar line to pump (not shown) shows very little Er signal. The shorter wavelength pump has a higher absorption coefficient, reducing the amount of Er in the excitation volume. To increase the Er signal, the Er should be implanted at lower energies so it is closer to the surface. Other possibilities include the addition of oxygen, which has been shown to increase Er PL in c-Si [4], or a different excitation method, e.g. electroluminescence, could be used.

CONCLUSIONS

Erbium photoluminescence has been observed in ion-implanted pure a-Si. In addition, a broad luminescence attributed to defects in the a-Si is present. Annealing at temperatures up to 500°C increases this intrinsic background. A 400°C anneal is required to observe the Er signal. The fluorescence lifetimes of the Er and the background are both less than 150 μsec under all anneal conditions. Although it is easy to introduce Er concentrations in a-Si well in excess of the c-Si solubility value, the low PL signal and short fluorescence lifetime suggest that Er-doped ion-implanted a-Si may be impractical as an optical material.

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