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Hydrogenated amorphous silicon with small amounts of erbium (Er/Si concentration ~5 at. %) was prepared by radio frequency sputtering from a Si target partially covered by tiny metallic Er chunks. Four sets of samples were studied: nonintentionally contaminated hydrogenated and nonhydrogenated amorphous silicon-erbium (a-SiEr:H and a-SiEr); nitrogen doped a-SiEr(N):H and oxygen contaminated a-SiEr(O):H. Samples from the first two sets present only faint 1.54 μm photoluminescence characteristic from Er^{3+} ions even at 77 K. Samples from the other sets show this luminescence at 77 K as deposited, without any further annealing step. Thermal annealing up to 500 °C increases the photoluminescence intensity, and room temperature emissions become strong enough to be easily detected. These results indicate that in an amorphous silicon environment the chemical neighborhood of the Er^{3+} ions is crucial for efficient 1.54 μm emission. Raman scattering from both as-deposited and annealed samples showed that network disorder relaxation by annealing is not determinant for efficient Er^{3+} luminescence. © *1997 American Institute of Physics.* [S0003-6951(97)03803-5]

The study of erbium impurities in silicon has received enormous attention in recent years.[1] Much of this interest stems from the possibility of achieving silicon-based electro-optical devices.[2–4] Rare earth trivalent ions in some solid compounds emit light at characteristic wavelengths due to an internal 4f transition. This emission is quite independent from the host, and is observed in many different materials. In the case of Er^{3+}, the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition corresponds to 1.54 μm, the wavelength at which standard silica-based optical fibers present their minimum transmission loss. This transition is dipole forbidden in the free atom. Only when the crystal field of the host breaks inversion symmetry and mixes states of opposite parity the transition is allowed. Several works were focused on the study of ion-implanted crystalline[5,6] and amorphous[7] silicon and a few studied amorphous films prepared by codeposition, either simultaneous[8] or sequential.[9] In this letter, we report on a-SiEr:H thin films prepared by cosputtering from a partially erbium covered silicon target. The 1.54 μm luminescence was studied in nonintentionally contaminated hydrogenated and nonhydrogenated amorphous silicon-erbium (a-SiEr:H and a-SiEr); nitrogen doped a-SiEr(N):H and oxygen contaminated a-SiEr(O):H as a function of annealing processes. We found that the presence of impurities (either O or N) is essential for the observation of efficient Er^{3+} related luminescence. We could also establish that high temperature annealing enhances this luminescence without significantly changing the overall network disorder.

All samples (~1 μm thick) were prepared by radio frequency sputtering from a 3 in. diam 99.999% Si target partially covered by small metallic 99.9% Er platelets (~0.025 cm^2 each). The surface coverage (~2%) was the same for all samples. The sputtering yield for Er is approximately 1.5 times higher than that for Si under the deposition

conditions,[10] so the erbium-to-silicon (Er/Si) concentration in the samples can be estimated to be roughly ~3 at. %. The Er concentration was cross checked by x-ray photoelectron spectroscopy (XPS) measurements exciting with the Mg K_α line. The photoelectron yield for the Er 4d and 4p core levels (0.12 and 0.24, respectively) are one order of magnitude higher than that of Si 2s and Si 2p levels (0.018 and 0.019).[11] Unfortunately, the Er 4d core level energy coincides with the Si plasmon and the Er 4p core level energy coincides with the Ar 2s core level, rendering XPS very difficult to interpret. In order to check the Er concentration, we prepared a sample with ~6% Er-to-Si surface coverage, and measured Er/Si of 11±1 at. %. This result is in excellent agreement with the estimation from the surface coverage. The other parameters which were common to all samples were: sputtering gas (Ar); substrate temperature (200 °C); total gas pressure (10 mTorr); total gas flux (~200 sccm); cathode bias (700 V). Hydrogenated samples were prepared adding 1 mTorr partial H_2 pressure to the sputtering gas. Nitrogen doped samples were made by adding 0.05 mTorr of electronic grade N_2. This corresponds to a N/Si concentration of ~1 at. % measured by nuclear reaction analysis.[12]

Oxygen contaminated samples were obtained by preparing a-SiEr:H films under lower cathode bias. When prepared under these nonoptimum conditions, the samples have columnar morphology. They acquire a stable O/Si concentration of ~3 at. % (measured by infrared absorption spectroscopy) during the first few minutes of exposure to ambient atmosphere.

Photoluminescence (PL) was measured at room temperature and 77 K with the samples placed in a liquid nitrogen cryostat. It was excited by the 514.5 nm line from an Ar^+ laser (40 mW), dispersed by a 25 cm monochromator, and detected by a liquid-nitrogen cooled Ge detector using standard in-phase techniques. Raman scattering measurements used the same laser line (200 mW), an 85 cm double mono-

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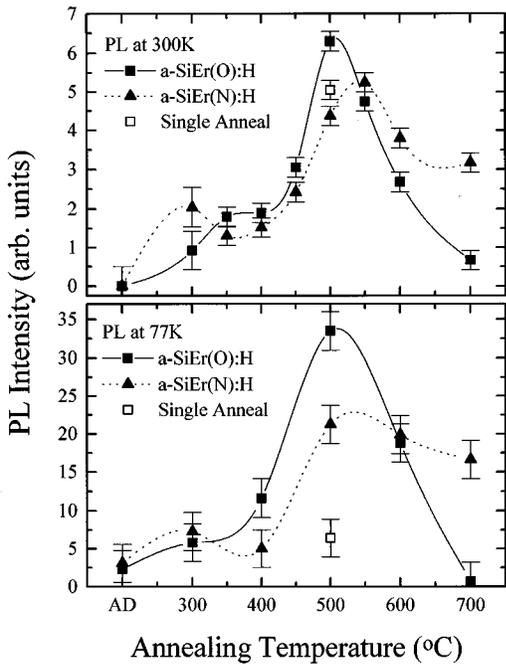[a)]Electronic mail: zanatta@ifqsc.sc.usp.br

FIG. 1. Er^{3+} PL intensity vs annealing temperature for a-SiEr(O):H (squares) and a-SiEr(N):H (triangles). The full squares correspond to cumulative annealing and the empty squares correspond to single annealing. The measurement temperatures are indicated.
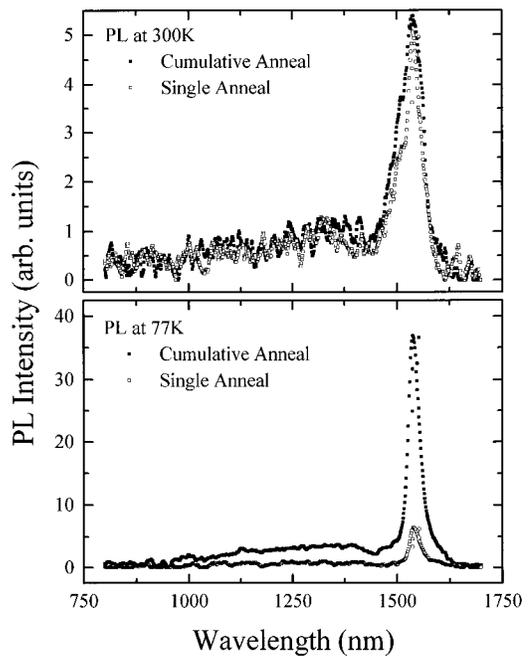

FIG. 2. Er^{3+} PL spectra for a-SiEr(O):H submitted to cumulative (CA) annealing up to 500 °C (full squares) and single annealing at 500 °C (open squares).

chromator, a cooled photomultiplier, and photon counting techniques. Thermal annealing was done by leaving the samples for 15 min at the desired temperature (between 300 and 700 °C) in a quartz tube furnace under pure argon flow.

Nonintentionally contaminated samples did not present detectable Er^{3+} PL without thermal annealing. Even after annealing at 700 °C this luminescence is detected only at 77 K and is very weak, being slightly stronger in hydrogenated samples.

Both N doped and O contaminated samples presented Er^{3+} PL at 77 K as-deposited. Cumulative thermal annealing (CA), i.e., repeated annealing steps at increasing temperatures for the same specimens, increased the 77 K PL intensity and allowed detection of room temperature PL. The dependence of the PL intensity on CA at increasing temperatures for one sample of each set is represented in Fig. 1. The maximum light emission is found at 500 °C for both samples. In order to investigate whether the annealing process depends on the thermal history of the samples, one previously unannealed a-SiEr(O):H sample was submitted to a single anneal (SA) of 15 min at 500 °C, the temperature for which CA luminescence reaches its maximum. The PL intensity for SA was found to be a factor 5 smaller than CA for measurements at 77 K and comparable for measurements at room temperature. The PL spectra for these samples are represented in Fig. 2.

Raman scattering data for as-deposited, CA and SA a-SiEr(O):H samples are represented in Fig. 3. The half-width at half-maximum of the TO vibration mode (Γ_{TO})is associated with the distribution of bond angles in tetrahedrally coordinated amorphous alloys.[13] In the as-deposited sample Γ_{TO} is 86 ± 2 cm^{-1}, while for the CA and SA samples Γ_{TO} is 82 ± 2 and 80 ± 2 cm^{-1}, respectively.

The absence of Er^{3+} PL in nonintentionally contaminated samples can be understood considering the short range order of a-SiH. In a-Si:H the first near neighbor is almost at the same position as in its crystalline counterpart, with virtually no distortion in the bond lengths and very small distortions in the bond angles.[14] This provides a chemical environment for the Er^{3+} ions which is very similar to that found
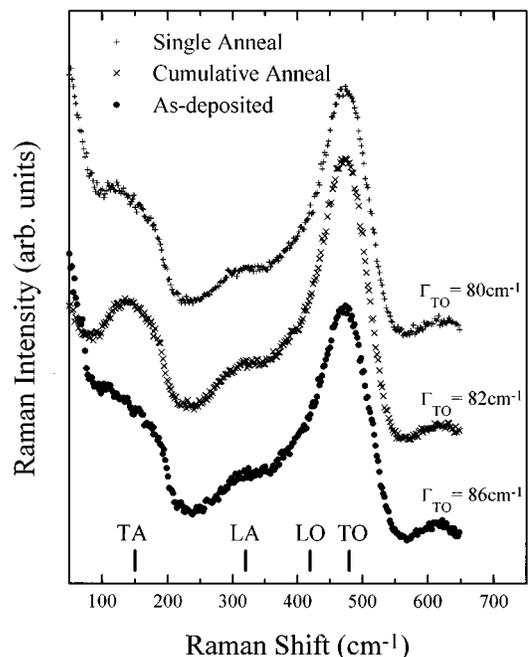

FIG. 3. Raman scattering at room temperature from a-SiEr(O):H samples. The spectra have been vertically shifted for clarity. TA, LA, LO, and TO stand for the vibration modes present in an amorphous network and correspond to the transverse and longitudinal acoustic, and longitudinal and transverse optical modes, respectively.

in pure crystalline silicon. It has been argued[15] that Er in a pure crystalline silicon matrix assumes the optically inactive 12-fold coordination. In the neighborhood of O (or other light impurities), Er^{3+} can assume a luminescent noncentrosymmetric 6-fold configuration. Our a-SiEr and a-SiEr:H have nonintentional impurity levels below 10^{16} cm^{-3}, providing a very small probability of formation of luminescent Er^{3+} sites. Only after high temperature (700 °C) annealing a significant fraction of the impurities reached Er atoms to form these optically active sites.

The PL intensity data of Fig. 1 are qualitatively similar to those reported in the literature for Er^{3+} in both crystalline[16] and amorphous[7] Si hosts. The details of the dependence of the PL intensity on the annealing temperature, however, depend on the matrix characteristics and on the incorporation conditions. The maximum PL efficiency is found when: (1) the number of active Er^{3+} sites is maximum, (2) the excitation transfer rate from the host is maximum, and (3) the nonradiative de-excitation rate is minimum. The increase of efficiency up to 500 °C and its decrease for higher annealing temperatures is probably determined by the condition 1. In sputtered a-Si:H prepared under low bias as our a-SiEr(O):H samples, most of the hydrogen outdiffuses at temperatures below 400 °C. Thus, when the Er^{3+} PL reaches its maximum, the density of dangling bonds is already near the saturation value for these materials. Si dangling bonds are very effective nonradiative recombination centers in a-Si:H. That the maximum of the Er^{3+} PL occurs when the density of dangling bonds is very high indicates that the density of active Er^{3+} ions in our samples is even higher, making the condition 2 not determinant. For a given excited electron, the average probability of being captured by an Er^{3+} state is much higher than the probability of being captured by a Si dangling bond. At low temperatures, the de-excitation rate of Er^{3+} centers is very small, rendering condition 3 not significant. Notice that the CA sample not only shows strong Er^{3+} PL, but also a weaker broad PL band centered near 1.3 μm (Fig. 2). This PL band is associated to radiative recombination at Si dangling bonds,[17] found both in low quality and in doped a-Si:H. In the SA treatment, the outdiffusion of hydrogen is much less effective, not leaving enough dangling bonds to yield significant radiative recombination. The processes involved in the activation of Er^{3+} are also less effective in SA.

At room temperature, the Si dangling bond PL is not detected, and the Er^{3+} PL intensity is almost independent of the thermal history. This indicates that the limiting process is the same for both samples. Since they exhibit very different Er^{3+} PL efficiencies at low temperatures, this limiting process is most probably the mechanism 3. This process may be qualitatively similar to the quenching of a-Si:H PL at room temperature.[18]

The decrease of the Er^{3+} PL signal for CA above 500 °C for all samples could be due to thermally activated outdiffusion of the impurities which form the proper environments for Er^{3+} PL. Since N impurities are better bonded than O impurities (they were introduced during deposition rather than by a room temperature postreaction) the outdiffusion of the former is less efficient than the latter. This could be the reason for a different decrease in the Er^{3+} PL signal with CA

above 500 °C in N doped and in O contaminated samples.

An important characteristic of cosputtering a-SiEr:H is that in this material not only the presence of O but also N can enhance Er^{3+} luminescence in similar ways. This was reported for coimplanted Er and N in crystalline Si.[19]

The enhancement of the Er^{3+} PL with annealing in Er implanted crystalline Si amorphized by the implantation has been partly attributed to the network structural relaxation and defect annealing.[16,20] Raman scattering from our samples indicates that in a-Si:H this is not the case. Both CA and SA reduce Γ_{TO} by the same amount indicating that as far as structural disorder is concerned both CA and SA produce the same effects in these amorphous hosts. However, the intensity of the Er^{3+} PL peak at 77 K is 5 times stronger for CA. This indicates that the chemical environment is much more important than structural disorder for the occurrence of Er^{3+} luminescence.

In conclusion, we have observed Er^{3+} related PL in hydrogenated amorphous silicon-erbium hosts prepared by cosputtering. This luminescence was only observed in intentionally O contaminated or N doped samples. Our data indicates that N might have an effect similar to that of O for Er^{3+} activation. Raman scattering results indicated that the structural relaxation induced by thermal annealing is not the determinant parameter for efficient Er^{3+} related luminescence.

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