

Room-temperature silicon band-edge photoluminescence enhanced by spin-coated sol–gel films

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Photoluminescence is observed at room temperature from phonon-assisted band-to-band emission in Si (1.067 eV peak) using unpatterned bulk p-type silicon wafer samples that were spin-coated with Er-doped (6 at.%) silica-gel films (0.13 μm) and vacuum annealed; the strongest emission was obtained at ~ 700 °C. Comparative study of annealing behavior indicates an efficiency enhancement of two orders of magnitude. Emission from Er^{3+} ions in the silica film is used to gauge relative emission strengths. Mechanisms for inducing emission from silicon utilizing stresses in sol–gel films are discussed.

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Producing light emission from silicon at room temperature generally entails selecting structures and materials to circumvent the inherent disadvantages of the indirect Si band gap (e.g. typical 10^{-4} quantum efficiency at 300 K [1]; see also [2]) [3]. Previous methods include selection of float-zone Si with high minority carrier lifetime [4], nanostructured p–n junctions [5], oxidized porous Si [6], Si nanocrystals embedded in suboxide [7], ultra-thin Si crystal (silicon on insulator or SOI) [8,9], nanopatterned SOI [10], and p–n junctions formed by ion implantation [11–14], diffusion doping [14] or amorphous-Si heterostructures [15]. This work reports enhancement of near-band-edge 1.067 eV (1162 nm) emission at room temperature by spin-coating and annealing sol–gel silica films on bulk Si without employing any of these silicon-material manipulations. Enhanced Si emission is shown to be correlated with inhomogeneous film stresses.

The silica films were doped with erbium for the purpose of producing IR emission using common Si wafers as substrates. Consequently, photoluminescence (PL) spectra show the expected optical activity in the 1535 nm band (~ 0.807 eV) from Er^{3+} ions in the silica

film (intra 4f band $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions), in addition to emission from the Si substrate (1.067 eV peak). Room-temperature emission from Si in association with sol–gel films (whether Er doped or not) appears to be unreported in prior work.

Samples for this study were made from 2.5 cm pieces cut from 150 mm Czochralski (CZ) Si wafers (Semiconductor Wafer, Inc.) of the following specifications: boron-doped p-type, 3–30 Ωcm , $\langle 100 \rangle$ orientation, single-side polished, 675 ± 25 μm thick (minority carrier lifetime in a CZ Si wafer is typically rather short, ~ 50 μs). The Si was cleaned with an RCA process. Prior to mounting in a spin-coater, the Si substrates were cleaned with acetone, methanol and deionized water, and blown dry. The spin-coating solution was prepared using a sol–gel recipe: 0.5 g high-purity Er_2O_3 powder was dissolved in a solution of 4 ml ethanol, 4 ml acetic acid and 1.6 ml deionized water, and stirred at 45 °C for 3 h; 2 ml $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) was added and stirred at 80 °C for 10 min. The resulting sol was applied through a 0.45 μm syringe filter onto Si in a spin-coater (1200 rpm, 30 s). The samples were then oven dried in air at 120 °C for 30 min and subsequently annealed in a horizontal vacuum furnace (2 Pa, 1 h) at temperatures, T_a , ranging from 500 to 950 °C. PL spectra were recorded by a model Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) with a double-excitation monochromator (Xe lamp source), single-emission

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monochromator, and cooled InGaAs photodiode (Hamamatsu), in the wavelength range 850–1600 nm (data converted to energy: 0.775–1.459 eV). The excitation wavelength (522 nm) was determined for maximizing Er^{3+} emission.

PL spectra are shown in Figure 1 for two samples, A and B, that were annealed at T_a of 700 and 850 °C, corresponding to the solid and broken curves, respectively. The data show two major peaks at 0.807 and 1.067 eV. The 1.067 eV peak is strongest for annealing at 700 °C (sample A), where it is enhanced 50-fold when compared to unannealed, air-dried films. This emission is associated with the Si substrate (as verified below). Silica film thickness of 0.13 μm (25% shrinkage upon annealing, as is typical [16]) and refractive index of 1.471 at 630 nm was measured for sample A. The 0.807 eV peak is strongest for annealing at 850 °C (sample B, left dot-dash curve, scaled by a factor of 1/6), and is associated with emission from Er^{3+} in the silica film. Weaker emissions in the region 1.25–1.35 eV are attributed to $^4I_{11/2} \rightarrow ^4I_{15/2}$ transitions in Er^{3+} . The annealing temperature for sample B corresponds to maximum 0.807 eV Er^{3+} emission and is near that used for similar Er-doped sol-gel silica films (~ 900 °C [17]). On comparing the two emission signals, the peak emission from the Si (sample A at 700 °C) is about 16% of the peak emission from Er^{3+} (sample B at 850 °C); from areas under the respective spectra, the integrated signal from the Si is 50% of that from Er^{3+} .

Included in Figure 1 (dotted curve) is a one-phonon (i.e. dominant phonon) model for emission of photons at energy E by phonon-assisted recombination of free electrons and holes in Si, represented by the expression, $\text{PL}(E) \propto (E - E_0)^2 \exp[-(E - E_0)/k_B T]$ (uncorrelated pair model; see e.g. [15]); it is calculated with threshold energy $E_0 = 1.020$ eV and thermal energy $k_B T = 0.023$ eV. Since the dominant phonons are the momentum-conserving transverse optical phonons of energy $E_{\text{ph}} = 0.0578$ eV, the effective band gap, neglecting possible corrections for exciton binding or trapping, is $E_G = E_0 + E_{\text{ph}} = 1.078$ eV, which is about 42 meV below the intrinsic Si

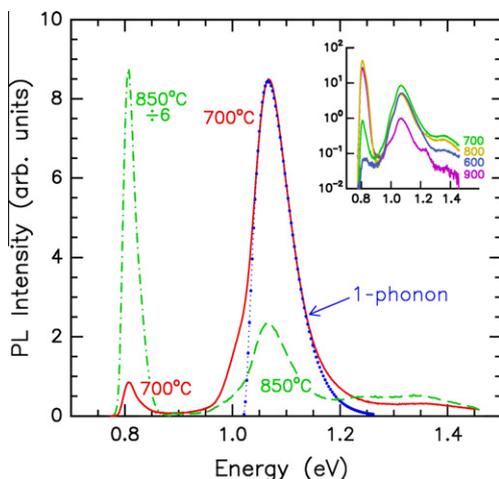


Figure 1. Photoluminescence intensity spectra from samples of Er-doped sol-gel films on Si annealed at temperatures of 700 °C for sample A, solid curve; and 850 °C for sample B, broken curves (left dot-dash portion divided by 6). Dotted curve shows Si one-phonon component for sample A. Inset: PL spectra (semi-log scale) at indicated annealing temperatures (°C).

band gap (1.12 eV). Although this is an approximate examination of the data (weaker phonon components, e.g. features appearing below 1.03 eV, were not included because they commingle with Er^{3+} emissions), the reasonable overlap for much of the PL signal peaking at 1.067 eV indicates that this emission most likely originates from the Si substrate and not from the film. The inset to Figure 1 presents PL spectra on semi-log scales, showing similarity in exponential form ($E > E_0$) at the various T_a . The X-ray diffraction, not shown, of sample A shows no evidence of polycrystalline Si (e.g. absence of Si nanocrystals within the deposited film [3]).

Variation of the peak Si emission intensity with annealing temperature is presented in Figure 2, illustrating that emission is strongest for $T_a \approx 700$ °C. The PL is appreciable (up to 50% of the maximum) for 600–800 °C and becomes rather weak for $T_a < 600$ °C (PL increases 5% from air-dried to $T_a = 500$ °C); PL is again low for $T_a > 900$ °C. The inset to Figure 2 is a plot of the peak PL intensities at ~ 1.067 eV vs. those at ~ 0.807 eV; the implicit variable T_a increases in clockwise rotation, 500 °C being at the lower left (Er^{3+} PL for air-dried films is obscured by noise and is therefore excluded). Linear fit to data logarithms, not shown, yields slope of 0.10 ± 0.17 , i.e. near zero, and a coefficient of linear correlation 0.9381. For the five samples yielding substantial ~ 1.067 eV emission (with emission levels varying by less than a factor of 2), the Er^{3+} emission increases from near weakest to near strongest (with values varying by a factor of 600). The strength of the emission from the Si therefore does not depend on that from the Er^{3+} in the silica film, from which we conclude that emissions at these two wavelengths arise from independent mechanisms. Emission at both wavelengths displays a maximum in the dependence on T_a (700 °C for the 1.067 eV peak, 850 °C for the 0.807 eV peak), hence the data points in the inset of Figure 2 execute a cyclical pattern.

The observed annealing behavior points to enhancement of emission from the Si through its interaction with the sol-gel film. Annealing sol-gel films for $T_a \approx 500$ °C removes virtually all of the solvents, organic compounds and water, but leaves residual hydroxyls, which are detected by IR absorption signatures [18,19]. Films annealed at higher T_a become denser, hydroxyl

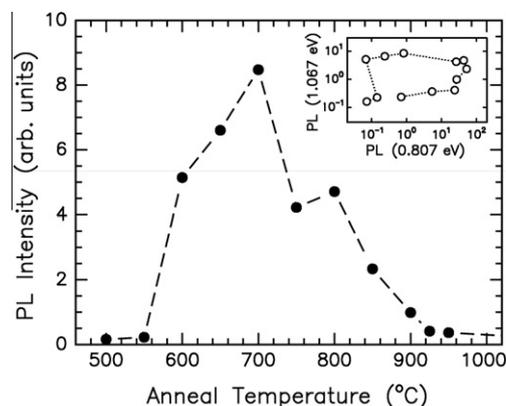


Figure 2. Peak photoluminescence intensities (~ 1.067 eV) from samples of Er-doped sol-gel films on Si as function of annealing temperature. Inset: PL peaks at 1.067 eV vs. 0.807 eV (dotted lines indicate annealing temperatures, increasing clockwise).

content decreases and porosity is reduced [16,20,21]. In Figure 3 we show the IR transmittance of five samples for $500\text{ °C} \leq T_a \leq 900\text{ °C}$ (these samples were in the ambient for an extended period prior to measurement). The cut-off in transmittance below 1000 nm is due to free carrier excitation in the Si substrate. Transmittance above 1200 nm is determined by film thickness and refractive index, as well as by variability in backside Si reflectance among the samples, owing to the use of single-side polished wafers. Structure is seen in the regions 1360–1480 and 1650–1760, which are close to where absorption from overtone vibrations of adsorbed water is observed in annealed monolithic silica gels [22]; the transmittance dip at 1720 nm (identified with overtone OH stretching vibrations in H-bonded H₂O [21]) is most pronounced for the sample annealed at 700 °C.

Accepting that the near band-gap emission originates from a modification of the Si substrate, perturbation in the semiconductor bands in some form is worth bearing in mind. Formation of shallow p–n junctions by surface diffusion, as in the dopant diffusion method of Ref. [14], appears improbable in this case, since high-temperature diffusion from an Er-doped sol–gel film has been determined to be insufficient for doping Si with Er [23], owing to low solid solubility and diffusivity of Er in Si (note: the sol–gel films contain only Er as a potential dopant to underlying substrate). The results also indicate that the PL is not caused by damage in the Si, such as produced in the ion-implantation method [11,12]. Once formed, extended topological defects, dislocations and stacking faults are rather stable under annealing up to 950 °C, and hence any PL signal that might associated with them persists rather than following the observed trend of annealing away (Fig. 2).

Inherently reversible perturbations in the Si substrate, on the other hand, can be induced by oxide defects and stress. Pure-silica sol–gel films are known to be electrically leakier and have higher densities of interface states than their thermally grown counterparts, and these electronic qualities improve with increasing annealing temperature [24,25]. Annealing in air yields

better oxides than annealing in vacuum or dry N₂, which could simply be due to passivation of the Si surface by thermally grown oxide. Although reductions in oxide and interface defects could account for the decreased PL observed for $T_a > 800\text{ °C}$, it is difficult to apply similar reasoning to $T_a < 600\text{ °C}$, since sol–gel films are comparatively more defective at lower T_a .

Stresses in sol–gel films, caused by shrinkage and porosity, are the more likely substrate interactions to consider, especially since silica gel is known to have inhomogeneity stemming from the fractal polymerization of SiO₂ in sol–gel hydrolysis [16,21]. Thermal densification produces large stresses [21], particularly for annealing above 400 °C, where mean tensile stress on the order of $\sim 0.5\text{ GPa}$ has been determined for sol–gel films on Si wafers [20]. Film stresses reduce the frequency and increase the width of IR absorption from asymmetric Si–O–Si stretching vibrations (TO₃ modes, 1060–1080 cm⁻¹) [21], which are interpreted as decreased and more broadly distributed tetrahedral bond angles. In a prior study of spin-coated sol–gel films on Si (similar to the present process, except for the Er doping), the lowest frequency and greatest broadening of the TO₃ mode occurred for annealing at $T_a = 700\text{ °C}$ [20] (IR line width data reproduced in Fig. 3, inset), which coincidentally is where the strongest Si PL from our samples is observed. These IR data also indicate that bond-angle distortion decreases at high temperatures ($T_a \geq 900\text{ °C}$), where glassy reflow allows stress relief in SiO₂ films. Given that Si PL is comparatively subdued for $T_a < 600\text{ °C}$ as well as for $T_a > 900\text{ °C}$, one may conclude that enhanced PL at $T_a \approx 700\text{ °C}$ is associated with non-uniformities in film stresses, rather than with large mean film stress alone.

Inhomogeneous film stresses, acting in concert with native interfacial roughness, is therefore expected to create random elastic strains in the Si, produce random shifts in electron and hole bands, and modulate the Si band gap. A similar scenario of band-gap fluctuations was previously invoked to explain enhanced Si emission from implanted (and presumably also diffused) junctions, by virtue of inhomogeneities (“doping spikes”) at dopant (B or P) concentrations near the solid solubility limit [13]. According to this mechanism, free carriers are released by excitons trapped at defects owing to energy band distortions. (Alternative explanations have been proffered, such as large strains near dislocations [11] and gettering effects of defects formed by the implant-anneal process [12]; however, these do not account for enhanced emission observed in dislocation-free diffused junctions [14].) Thus it is reasonable to surmise that the random strains in Si adjacent to sol–gel films produce localized band fluctuations, analogous to those from doping spikes, and are sufficient to increase the effective cross-section for radiative free-carrier recombination. Applying this interpretation, enhanced emission is expected to be produced in only a thin layer at the Si surface (on the order of the film thickness, $\sim 0.1\text{ }\mu\text{m}$, or less); since the excitation radiation penetrates $\sim 1\text{ }\mu\text{m}$, quantum efficiency (QE) could actually be increased $\sim 10^3$ -fold (i.e. $\sim 10\times$ larger than the observed enhancement), suggesting $\text{QE} > 1\%$ (assuming $\text{QE} \leq 0.01\%$ for CZ Si [1,2]).

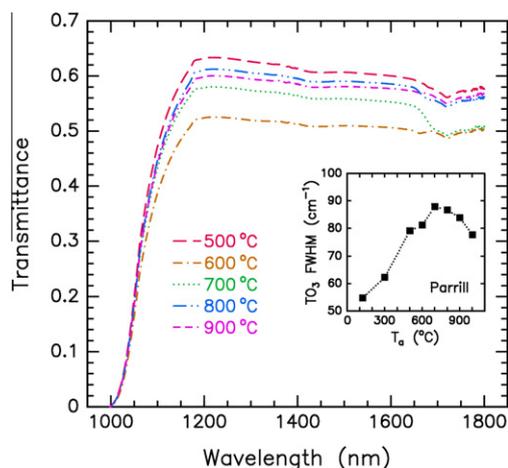


Figure 3. Infrared transmittance for samples of Er-doped sol–gel films on Si annealed at temperatures indicated. Inset: full-width at half-maximum of TO₃ vibrations in undoped sol–gel silica films on Si (from Ref. [20]).

The position of the PL peak (1.067 eV) is at a slightly lower energy than that observed for implanted Si (1.081 eV) [12] or in mesoscopic oxidized porous Si (1.088 eV) [6], which suggests a slightly smaller average band gap. More closely related to the present study are structures comprising thin islanded Ge films grown epitaxially on Si as well as on thin Si–Ge alloy buffer layers; both types yield room-temperature PL from the Si substrate (~ 1.065 eV peak), in addition to emissions at lower photon energies from the Ge islands [26]. Such films contain a strain pattern created by the Ge–Si lattice mismatch and islanded growth topography; the PL does not involve forming p–n junctions, as in this work. Our data also show that the sample for $T_a = 700$ °C yields both the strongest Si PL (Fig. 2) and the most pronounced IR absorption features (Fig. 3). This is consistent with IR signatures of hydration in sol–gel films (on Si), which have been correlated with high film stress [20].

In conclusion, near-band-gap (1.067 eV) PL at room temperature has been observed in CZ Si wafer material by spin-coating and annealing sol–gel silica films doped with Er (emitting at 0.807 eV). Emission from the Si, which was strongest for annealing at 700 °C, correlates with inhomogeneous stresses in sol–gel films (owing to strong 25% shrinkage), as indicated indirectly by IR absorption. Based on the independent annealing behavior of the two PL signals and comparison with prior studies of sol–gel film properties, it appears that the Er is not directly involved in the Si emission. The spin-coating process presented herein is notable for enhancing light emission from bulk-type Si (estimated QE $\approx 1\%$) in the absence of any patterning or p–n junctions.

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