Enhancement and stabilization of porous silicon photoluminescence by oxygen incorporation with a remote-plasma treatment

Y. Xiao,[a] M. J. Heben, J. M. McCullough,[b] Y. S. Tsuo, J. I. Pankove,[a] and S. K. Deb
Basic Sciences Division, National Renewable Energy Laboratory, Golden, Colorado 80401

We report a treatment that enhances and stabilizes the photoluminescence (PL) from porous Si films. Films prepared by anodization in a 50% HF/ethanol solution were annealed at 450 °C in vacuum, exposed to air, and then exposed to a remote-hydrogen plasma. Infrared absorption spectroscopy revealed that the concentration of oxygen, rather than hydrogen, was increased by the processing steps, and that silicon dihydride species had been eliminated from the surface. The PL from a treated film was initially ∼30 times more intense than from the as-etched films. The PL intensity increased with illumination time in air until a steady-state intensity was reached.

Recent reports of visible photoluminescence (PL) from porous Si (PS) have stimulated considerable interest in the scientific community,[1,2] and suggest that the material will have uses in optoelectronic applications. Unfortunately, the physical mechanisms responsible for the PL are not well understood, and the emission normally degrades with time in oxygen- or moisture-containing environments.[3,4] infrared absorption spectroscopy (IR) has shown that the PL intensity is strongly correlated with the concentration of silicon dihydride (SiH_2) surface species,[5,6] and that the PL degrades with illumination time due to the incorporation of oxygen-containing species.[3] Other studies have shown that oxygen incorporation can result in a stabilized PL emission at ∼1/3 of the initial intensity,[7] or enhance the PL by as much as a factor of 10.[8] Evidently, the manner in which oxygen is incorporated onto PS surfaces dictates whether a beneficial or detrimental function is performed.

We report a procedure that incorporates oxygen into PS films and results in the enhancement and stabilization of the film's PL properties. The electrochemically etched samples were annealed in vacuum, exposed to air while PL and IR data were collected, and then exposed to a remote-hydrogen plasma. IR revealed that the concentration of SiH_2 was reduced by the vacuum anneal, while the concentrations of oxygen-containing species were increased at each stage of the procedure. Our data show that oxygen incorporation onto a PS surface populated by silicon monohydrides (SiH) produces chemical species that enhance the PL emission intensity. These species could serve to reduce the recombination velocity at the internal surfaces of the PS nanostructure, and thus enable a higher radiative recombination yield, or alternatively, be directly responsible for the luminescence in a role similar to that ascribed to siloxene.[9] Contrary to a suggestion made elsewhere,[6] our results demonstrate that SiH_2 terminations are not required for PS to emit intense visible PL. We also demonstrate that oxygen incorporation during the anneal/plasma treatment stabilizes the PL properties of PS against photochemical degradation.

PS samples were prepared from 3-in.-diam boron-doped (0.2 Ω cm) float-zone single-crystal Si wafers. Float-zone Si wafers have low as-grown oxygen content and are well-suited for studying the effects of process-incorporated oxygen. Aluminum electrical contacts were evaporated onto the backs of the p-type wafers. Electrochemical etching was performed in a cell that has been described elsewhere[10] with a 50% ethanol/50% HF (48 wt %) electrolyte. The anodization current was 10 mA/cm², and the etching time was 3 min. The resulting PS films were about 1.2-μm thick, and the PL was found to be quite uniform (±30% in peak intensity) over the nearly 3-in. diam.

The remote-plasma system consisted of a quartz tube connected to a mechanical pump and a diffusion pump with a liquid nitrogen cold trap. A resistively heated furnace was positioned concentrically outside of the quartz tube to heat the samples. Annealing was performed at 450 °C for 15 min in a vacuum of <1 mTorr. A capacitively coupled 100 MHz rf generator was operated at the minimum power (∼6 W) necessary to maintain a plasma within the tube. The PS samples were placed ∼10 cm from the nearest edge of the plasma to minimize damage by energetic ions and radicals. The 30-min remote-plasma treatments were performed in 0.1 Torr of flowing H_2 at 155 °C.

The room-temperature PL spectra of PS at various steps of the anneal/plasma treatment are shown in Fig. 1. The PL emission was excited by an Ar-ion laser operated at a wavelength of 488 nm, a spot size of 0.2–0.3 mm, and a power of 15 mW. The emitted light was dispersed by a spectrometer and detected by a RCA 31025 photomultiplier. The PL emission of an as-etched PS sample, which received a 20-s dip in 15% HF just prior to the measurement, is shown in Fig. 1(a). Though relatively weak in comparison to our brightest samples (*vida infra*), the spectrum displayed considerable intensity from 1.4 to 2.0 eV. The emission intensity was degraded when the as-etched sample was irradiated with the output of the Ar-ion laser
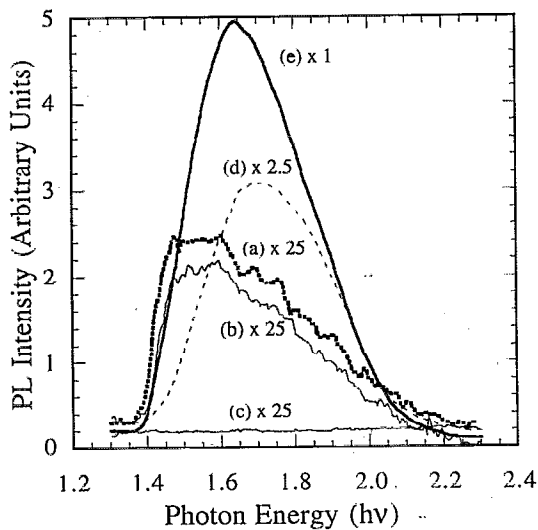
FIG. 1. Room temperature PL spectra of PS: (a) as-etched PS sample, (b) as-etched sample of part (a) after 20 min of light-soaking, (c) as-etched sample after 15 min anneal at 450 °C, (d) annealed sample after exposure to remote plasma for 30 min at 155 °C, (e) plasma-treated sample of part (d) after laser illumination for an additional 30 min.

for 20 min [Fig. 1(b)]. A subsequent annealing at 450 °C in vacuum for 15 min effectively quenched the luminescence [Fig. 1(c)]. Exposure of the sample to the remote plasma, as described above, recovered and enhanced the luminescence [Fig. 1(d)]. In comparison to the emission spectra of the as-etched sample, the peak intensity was increased by a factor of ~ 12 and the peak wavelength was shifted from 1.5 to 1.7 eV. The PL intensity increased further and was 50 times greater than that observed for the as-etched sample after the sample was irradiated with the Ar-ion laser for 30 min [Fig. 1(e)].

IR was performed at the different processing stages in order to monitor the changes in the populations of surface species (Fig. 2). The spectra were measured in transmission with a dual-beam Perkin–Elmer dispersive spectrophotometer and were referenced against a single crystal Si sample. Interference fringes in the data were removed by fitting the baseline to a ninth-order polynomial. The back-contact Al was removed before the IR measurement by rubbing with a HCl-soaked pad. Curve (a) displays the IR
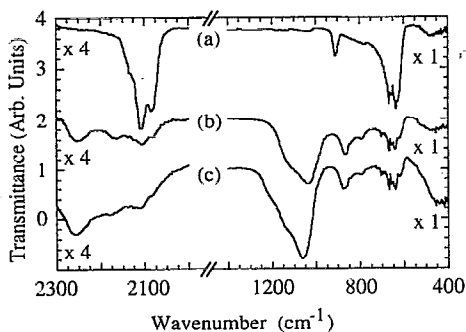

FIG. 2. IR data of PS at different processing stages: (a) as-etched with a 15–20 s HF dip, (b) annealed at 450 °C for 15 min; (c) annealed and then treated with the remote plasma at 155 °C for 30 min.

spectrum for an as-etched PS sample. Both the PS sample and the reference sample received a 15–20 s dip in 15% HF just prior to the IR measurement. The spectrum exhibits the expected vibrational modes for freshly prepared PS.[11] The SiH stretching mode at 2110 cm^{-1}, SiH_2 stretching and scissors modes at 2083 and 910 cm^{-1}, respectively, and SiH_n deformation modes between 610 and 670 cm^{-1} are clearly seen.[11] A small amount of oxygen was introduced during the preparation and/or transportation of the sample, and weak absorbances because of the stretching, bending, and rocking of O in the Si-O-Si group were found at 1035, 780, and 475 cm^{-1}, respectively. The occurrence of the Si-O-Si stretching mode at 1035 cm^{-1} suggests that oxygen was incorporated as a suboxide of the form $SiO_{1.5}$.[12]

In agreement with Gupta et al.[11] annealing the sample at 450 °C in vacuum decreased the hydrogen content in the sample [Fig. 2(b)]. Although a small absorption at 2083 cm^{-1} remained, the absence of a peak at 910 cm^{-1} revealed that SiH_2 species had been essentially eliminated from the surface. The reduction in intensity of the mode at 2110 cm^{-1}, and of the modes between 610 and 670 cm^{-1}, confirmed that the population of SiH had also been reduced. As observed by other researchers,[5,6] the removal of the dihydride species coincided with the disappearance of the PL from the sample [Fig. 1(c)].

The sample was exposed to air while acquiring the PL and IR data and, consequently, several new modes attributable to oxygen related species were found in the IR spectrum. A broad peak at 1036 cm^{-1} indicated that additional $SiO_{1.5}$ had formed on the PS surface.[12] The peaks at 870 and 2255 cm^{-1}, which have been observed in plasma-deposited films of hydrogenated silicon suboxides,[13] are associated with the $HSi-O_3$ bonding configuration. Similarly, the absorbance at 2170 cm^{-1} can be attributed to the $HSi-SiO_2$ structural group.

The 30-min remote-plasma exposure did not significantly alter the hydrogen content in the film [Fig. 2(c)]. Instead, unlike the work of Tsai et al.,[14] our treatment resulted in increased oxygen-related IR absorptions at 450, 870, 1060, and 2255 cm^{-1}, and the PL emission was greatly increased over that observed for an as-etched sample [Fig. 1(d)]. Our results also contrast with those of Khan et al.[15] where only 4% of the as-etched PL intensity was recovered after a presumably direct-hydrogen plasma treatment. The shift of the peak at 1036 [Fig. 2(b)] to 1060 cm^{-1} that accompanied the remote-plasma treatment is consistent with oxidation of $SiO_{1.5}$ to $SiO_{1.8}$.[12] The decrease of the intensity of the mode at 2170 cm^{-1} can be explained by a conversion of $HSi-SiO_2$ to $HSi-O_3$ with further oxidation. Suemune et al.[8] ascribed the appearance of modes at 2200 and 2250 cm^{-1} to the oxidation of SiH_x bonds in the photoirradiation treatment they employed to enhance (by $\sim 10\times$) the PL emission from PS. Our work is different in that we obtained a more complete oxidation of the SiH bond, as evidenced by the absorbance at 870 cm^{-1} [Fig. 2(c)], and that SiH_2 species were not prominent on our treated PS films. Moreover, we obtained an enhancement in PL emission of more than a factor of 100, as described below.
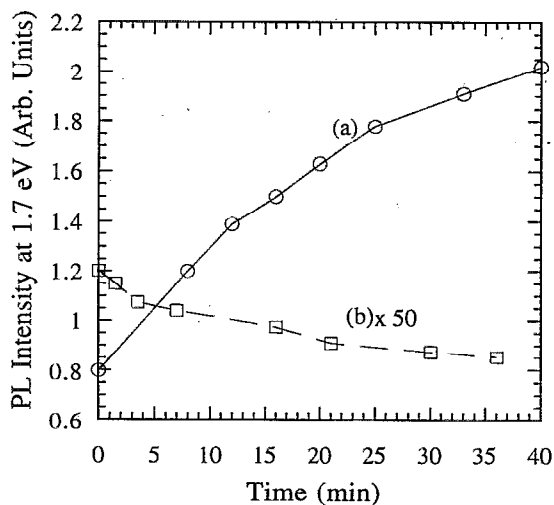
FIG. 3. Time dependence of PL emission intensity at 1.7 eV from PS illuminated in air by an Ar-ion laser: (a) plasma-processed sample, (b) as-etched sample.

There are several potential sources of oxygen in our remote-plasma process including oxygen in the residual gas in the system, oxygen adsorption by the annealed PS sample during transfer to and from the remote-plasma system, and oxygen or SiO_x removal from the interior of the quartz tube during the plasma treatment. Any of these sources could result in the generation of atomic oxygen within the plasma region. Although the density of atomic hydrogen in the plasma was much higher than that of atomic oxygen, the oxygen atoms should form a stronger bond with the PS surfaces.

Figure 3(a) shows the increase of the PL intensity at a photon energy of 1.7 eV while a sample was illuminated with the laser in air. In contrast, the emission at 1.7 eV from an as-etched sample decays with laser illumination [Fig. 3(b)]. In this comparison, the initial PL intensity was more than 30 times greater for the plasma-treated sample, and 120 times greater after both samples were irradiated for 40 min. After 3 weeks in air and ambient light, the PL emission reached a steady-state value that was an additional 50% stronger, and has continued to remain stable for more than 2 months. This stable intensity was more than 100 times higher than the initial PL intensities of the as-etched samples, and higher than the highest initial, unstable PL intensity that we have obtained in our laboratory using different sample preparation conditions (25% HF in methanol with a 0.5 mA/cm^2 current density for 90 min).

The anneal/plasma treatment clearly enhances the intensity and stability of the PL. This result is surprising considering that the IR spectra of the annealed and treated samples were only subtly different. The oxidation of suboxide species from $SiO_{1.5}$ to $SiO_{1.8}$, or the increase in the concentration of $H-SiO_3$, may provide surface terminations or chemical complexes that favor the PL mechanism. IR indicated that no new hydrogen was incorporated into the samples during the remote-plasma treatment. It is possible that atomic hydrogen had been incorporated, but in a form or quantity that was not detectable by IR spectroscopy. In this case, hydrogen could improve the PL behavior of PS by passivating electronic defects.

Brandt et al.[9] recently proposed that Si-O-H compounds derived from siloxene cover the surfaces of PS and are responsible for the PL. However, the IR spectra from our as-etched, float-zone Si sample does not display the intense Si-O related absorptions that are characteristic of siloxene.[9] Nevertheless, the as-etched sample produces considerable emission throughout the visible spectrum. PS surface passivation, either by incorporation of hydrogen species during electrochemical etching or by forming certain Si-O-H complexes, resulting in an increased radiative recombination efficiency within the PS nanostructure is consistent with the experimental results presented here.

In summary, we have discovered a treatment that enhances the PL emission from PS samples. The treatment produces PS films that emit visible luminescence even though the concentration of surface dihydrides is relatively low. After the remote-plasma treatment, laser irradiation in air produced a further increase in the PL intensity. The improved PL emission was stable even after long-term exposure of the PS to air, in sharp contrast to the behavior of as-etched or HF-treated PS. The incorporation of both oxygen and hydrogen in forming H-Si-O complexes can result in surface terminations that enable PS to emit intense and stable visible PL.

[1] V. Lehmann and U. Gösele, Appl. Phys. Lett. 58, 856 (1991).
[2] L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).
[3] M. A. Tischler, R. T. Collins, J. H. Stathis, and J. C. Tsang, Appl. Phys. Lett. 60, 639 (1992).
[4] E. Bassous, M. Freeman, J.-M. Halbout, S. S. Iyer, V. P. Kesan, P. Munguia, S. F. Pesarcik, and B. L. Williams, Mater. Res. Soc. Proc. 256, 23 (1992).
[5] M. B. Robinson, A. C. Dillon, D. R. Haynes, and S. M. George, Mater. Res. Soc. Symp. Proc. 256, 17 (1992).
[6] C. Tsai, K.-H. Li, J. Sarathy, S. Shih, J. C. Cambell, B. K. Hance, and J. M. White, Appl. Phys. Lett. 59, 2814 (1991).
[7] H.C. Chen, W. Wang, K. N. Manjularani, L. C. Snyder, and X. L. Zheng, Mater. Res. Soc. Symp. Proc. 256, 197 (1992).
[8] I. Suemune, N. Noguchi, and M. Yamanishi, Jpn. J. Appl. Phys. 31, L494 (1992).
[9] M. S. Brandt, H. D. Fuchs, M. Stutzmann, J. Weber, and M. Cardona, Solid State Commun. 81, 307 (1992).
[10] M. J. Hebcn, Y. Xiao, J. M. McCullough, Y. S. Tsuo, J. I. Pankove, and S. K. Deb, in Photovoltaics Advanced Research & Development Project, edited by R. Noufi (American Institute of Physics, New York, 1992), Vol. 268, pp. 421–427.
[11] P. Gupta, V. L. Colvin, and S. M. George, Phys. Rev. B 37, 8234 (1988).
[12] P. G. Pai, S. S. Chao, Y. Takagi, and G. Lucovsky, J. Vac. Sci. Technol. A 4, 689 (1986).
[13] D. V. Tsu,G. Lucovsky, and B. N. Davidson, Phys. Rev. B 40, 1795 (1989).
[14] C. Tsai, K.-H. Li, D. S. Kinosky, R.-Z. Qian, T.-C. Hsu, J. T. Irby, S. K. Banerjee, A. F. Tasch, J. C. Cambell, B. K. Hance, and J. M. White, Appl. Phys. Lett. 60, 1700 (1992).
[15] B. A. Khan, R. Pinker, K. Shahzad, and B. Rossi, Mater. Res. Soc. Symp. Proc. 256, 143 (1992).