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Photoluminescent thin-film porous silicon on sapphire

by

W.B. Dubbelday, Diane M. Szaflarski, R.L. Shimabukuro, S.D. Russell
and Michael J. Sailor

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Department of Chemistry
University of California, San Diego
La Jolla, CA 92093-0506

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13. ABSTRACT (Maximum 200 words) Results from the chemical stain etch fabrication and analysis of thin-film photoluminescent porous silicon on sapphire substrates are presented. The transparent sapphire substrate allows the excitation and collection of the luminescence at either the front or back of the wafer. Morphological differences found using scanning electron microscopy between porous SOS and porous bulk silicon are attributed to preferential etching of threading dislocations. This is confirmed by an observed stress relaxation in the Raman spectra. Also, it is shown for the first time that photoluminescent porous silicon (n-type) can be produced by photoinitiation of the chemical stain etch.			
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Photoluminescent thin-film porous silicon on sapphire

W. B. Dubbelday, Diane M. Szallarski,^{a) b)} R. L. Shimabukuro, and S. D. Russell
Naval Command, Control and Ocean Surveillance Center,^{c)} RDT&E Division, San Diego,
California 92152-5000

Michael J. Sailor

Department of Chemistry, University of California, San Diego, La Jolla, California 92093-0506

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Results from the chemical stain etch fabrication and analysis of thin-film photoluminescent porous silicon on sapphire substrates are presented. The transparent sapphire substrate allows the excitation and collection of the luminescence at either the front or back of the wafer. Morphological differences found using scanning electron microscopy between porous SOS and porous bulk silicon are attributed to preferential etching of threading dislocations. This is confirmed by an observed stress relaxation in the Raman spectra. Also, it is shown for the first time that photoluminescent porous silicon (*n*-type) can be produced by photoinitiation of the chemical stain etch.

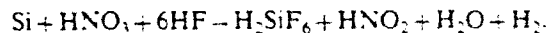
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Silicon on sapphire (SOS) is a proven technology for large scale integrated circuitry. It has several distinct advantages over bulk silicon for various applications. In electronic circuits SOS has intrinsically lower parasitic capacitances and provides better device isolation. It can be thinned to yield vertically scaled dimensions facilitating horizontal scaling of submicron devices. In addition the transparent sapphire substrate provides an ideal medium for flat panel displays and optical communication circuits.

With photoluminescent porous silicon¹⁻¹⁰ emerging as a potential electro-optic material for integrated circuit applications, a photoluminescent silicon-based material on a transparent substrate may have numerous applications in photonics-related technologies. In this work we show that luminescent porous silicon can be produced for silicon films as thin as 0.3 μm using a chemical stain etch of SOS material. The fabrication of thin-film porous SOS allows the elimination of interactions with and contribution from the bulk by etching the entire silicon layer. This aids in the elucidation of the photoluminescence mechanism by allowing the examination of the porous layer independently. The etching process can also be photochemically activated allowing the generation of photoluminescent patterns of porous silicon. The photoinitiated etching of porous features in silicon or SOS may be advantageous for VLSI processing.

The chemical stain etch used a solution of $\text{HF}:\text{HNO}_3$:deionized H_2O (1:5:10).^{11,12} Bulk (100)-oriented ¹¹B-doped silicon samples with 3–5 Ωcm resistivity were used. The SOS samples were epitaxially deposited silicon, boron doped *in situ* to $4 \times 10^{15}\text{ cm}^{-3}$, on 270 nm thick SOS ($1 \times 10^{18}\text{ cm}^{-3}$) to a total silicon thickness of 10 μm . The etch solutions were prepared by reacting a square centimeter of silicon with the $\text{HF}:\text{HNO}_3$ mixture for 2 min causing an accumulation of HNO_2 , the active oxidizer in the reaction.¹³ The chemical etch is a result of hole injection

from the HNO_3 oxidant into the silicon substrate via the following net reaction:¹³



The reaction is catalyzed by the presence of NO_2^- ions, and so there is usually an induction period observed for the etching process. Deionized H_2O was subsequently added to the solution prior to immersion of the sample to be etched. Typical etch times ranged from 1 to 15 min. The samples were rinsed with deionized water, dried with nitrogen and examined with a hand held ultraviolet (UV) lamp (Mineralight Model No. S52). Generally, samples etched for less than 1 min did not luminesce whereas SOS samples that are etched longer than ~ 15 min result in complete dissolution of the silicon off the sapphire substrate.

The photoluminescence spectra of etched samples were obtained using a defocused ($5\text{ mW}/\text{cm}^2$) 442 nm HeCd laser for excitation and the emission collected by a 1/4 m monochromator with a CCD detector. The collection spot size was on the order of 1 mm in diameter. Care was taken to record the emission spectra within 5 min of sample preparation in order to minimize the degradation of the luminescence which in some cases is observed with exposure to air. The porous SOS samples show photoluminescence signals comparable to those published for *p*-type bulk silicon.^{11,12} The photoluminescence spectra of 10 μm thick SOS etched for 9 min are shown in Fig. 1. The two curves shown are the emission spectra obtained when the sample is illuminated and emission collected at the silicon side (dotted line) and at the sapphire side (solid line) of the wafer. The photoluminescence maximizes in intensity at $\sim 700\text{ nm}$ with FWHM of $\sim 100\text{ nm}$. The luminescence from the Cr^{+3} impurity (695 nm) is pronounced in the sapphire side illumination spectrum. The similarity in the front and backside spectra suggests uniformity in the porous structure with depth, and that strain effects due to the lattice mismatch between the silicon and the sapphire are minimal.

Identically processed bulk porous silicon and porous SOS exhibit qualitatively different emission when illuminated with a UV lamp. Bulk porous silicon, chemically

^{a)} Postdoctoral Fellow from Office of Naval Technology administered by the American Society for Engineering Education.

^{b)} Present address: Molecular Biosystems Inc., San Diego, CA 92121.

^{c)} Formerly Naval Ocean Systems Center (NOSC)

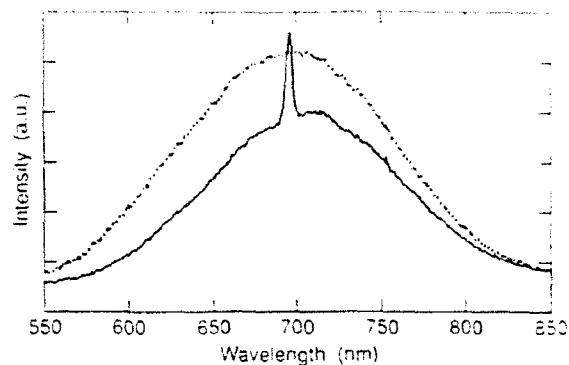


FIG. 1. The emission spectra of porous silicon on sapphire when illuminated at 442 nm. Results obtained by the excitation and collection of light from the front (silicon) side and the back (sapphire) side are shown with dotted and solid lines, respectively. Backside illumination and detection clearly shows the Cr^{3+} (695 nm) line from metal impurities in the sapphire.

etched as described above, emits a vivid luminescence, whereas the 10 μm thick porous SOS sample exhibits a hazy, diffuse luminescence emission. In order to understand these differences, the morphology of the samples were analyzed using scanning electron microscopy (SEM). The thickness of the porous layer in the bulk porous silicon is on the order of 100 nm with a surface roughness on the order of 10–20 nm. The porous layer on the SOS sample is less discernable, but shows a comparable surface roughness as shown in the SEM cross section in Fig. 2. Readily observable are additional crevices and cracks extending through the entire 10 μm silicon layer on sapphire. These cracks are attributed to preferential etching along threading dislocations and presumably cause diffuse scattering of the emitted photoluminescence. The dislocations arise from the thermal mismatch between silicon and the sapphire substrate which produces compressive stress in the silicon layer during the deposition at high temperature and subsequent cooling. This stress is partially relieved by the generation of threading dislocations. This hypothesis was examined using Raman spectroscopy to measure the strain-induced splitting and shift of the $\text{O}(\Gamma)$ phonon. Due to inversion symmetry in silicon's diamondlike structure,

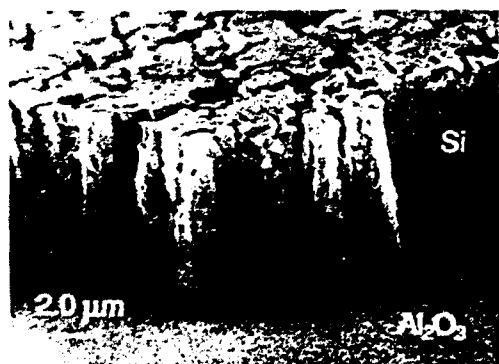


FIG. 2. Cross-sectional scanning electron micrograph with the sample tilted to show the top surface of chemically etched photoluminescent 10 μm thick silicon on sapphire.

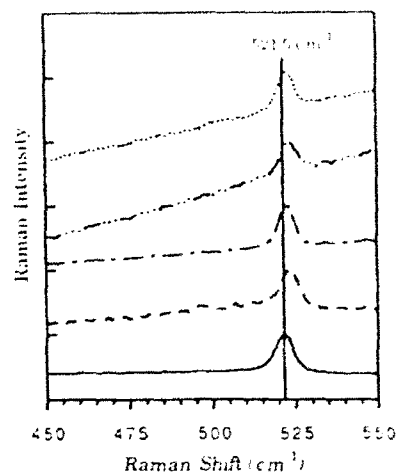


FIG. 3. Raman spectra of (solid) bulk silicon (dashed) 10 μm thick silicon on sapphire, (single dot/dashed) 10 μm thick porous silicon on sapphire (triple dot/dashed) 0.3 μm thick porous silicon on sapphire, and (dotted) porous Si prepared from a bulk (500 μm thick) wafer.

the optic modes are degenerate without stress.

Samples were mounted in a backscattering geometry, and contained in an argon ambient during data acquisition. Raman spectra were obtained using a 10 mW HeNe laser (632.8 nm) excitation source to minimize background photoluminescence generated by the porous samples. The inelastically scattered photons were analyzed in a SPEX Doublemate Spectrometer equipped with a photon counting CCD. The Stokes portion of the spectra are displayed in Fig. 3. The "solid" curve shows the $\text{O}(\Gamma)$ phonon of bulk silicon at $521.5 \pm 0.7 \text{ cm}^{-1}$ with respect to the excitation wavelength. This position is marked by a vertical line in the figure for reference. The "dashed" curve corresponds to an unetched 10 μm thick SOS wafer. The SOS exhibits a peak at $523.7 \pm 0.7 \text{ cm}^{-1}$, which corresponds to a compressive stress of $\sim 5 \times 10^9 \text{ dyne/cm}^2$.¹⁴ The "single-dot/dashed" curve is from a 10 μm thick SOS wafer etched to form a porous layer completely to the sapphire interface. This exhibits a peak at $522.2 \pm 0.7 \text{ cm}^{-1}$ consistent with the relaxation of stress in the etched porous silicon film. Similar results are obtained from a 0.3 μm thick SOS wafer also etched to form a porous layer completely to the sapphire interface and shown as the "triple-dot/dashed" curve.

Of particular note is the absence of features in the Raman spectra attributed to siloxene, amorphous silicon or microcrystalline silicon whose peaks occur between ~ 480 and 514 cm^{-1} (Refs. 15 and 16). Our analysis of the porous silicon layer on sapphire completely eliminates contributions from the bulk of the substrate, yet shows a peak position and linewidth (full width half maximum of $\sim 3 \text{ cm}^{-1}$) consistent with single-crystal silicon. The Raman spectra of porous silicon fabricated on a bulk (500 μm thick) wafer exhibits a peak at $522.2 \pm 0.7 \text{ cm}^{-1}$ which is shown in the "dotted" curve of Fig. 3. Differences in the crystalline properties may be attributed to the fabrication process, since previously reported Raman data were obtained on electrochemically prepared samples which may

enhance dissolution of the crystalline silicon under excessive current densities.

We have also demonstrated for the first time that photoluminescent porous silicon is produced via a photoinitiated chemical stain etch. For these experiments (100)-oriented bulk silicon, ^{75}As doped to 1–1.8 $\Omega\text{ cm}$ were used. The *n*-type SOS samples were epitaxially deposited silicon, phosphorus doped *in situ* (10^{15} cm^{-3}), on 270 nm thick SOS (^{75}As doped to 10^{18} cm^{-3}) to a total silicon thickness of 10 μm . The acid mixture of $\text{HF}:\text{HNO}_3$ was diluted with distilled H_2O (same ratios as above) and placed in optical quality cuvettes. The samples were immersed in solution and illuminated for 2–10 min using a 5 mW HeNe laser. For short times, typically 1 min, etching occurs only in the regions where the sample is illuminated. Patterns generated by double slit diffraction produced distinguishable etched features on the order of 30 μm with both the bulk and SOS material. As the illumination time increases the etching spreads out to regions of the silicon which were not illuminated and small etched features become washed out consistent with the generation of holes required for the catalyzation of the etching mechanism described above. After rinsing with deionized H_2O and drying with nitrogen, the samples display visible orange photoluminescence upon UV illumination. The porous silicon layer thickness is found using SEM to be $\sim 300\text{ nm}$ for samples irradiated for 8 min.

In conclusion, we have demonstrated photoluminescent porous silicon on sapphire (SOS). SEM and Raman data show a relaxation of the strained layer and photoemission by apparently crystalline material. Photoluminescence has been obtained from both the front and backside of the porous SOS material. We have also demonstrated a photoinitiated etch for the fabrication of photoluminescent po-

rous silicon whose mechanism relies on the generation of holes to catalyze the reaction.

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Naval Research Laboratory
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Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Professor John L. Stickney
University of Georgia
Department of Chemistry
Cedar Street
Athens, GA 30602

Dr. Stanislaw J. Szpak
Code 574
Naval Ocean Systems Center
San Diego, CA 92152-5000

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Department of Chemistry
Northern Illinois University
DeKalb, IL 60115

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Dept. of Chem. Engrg. & Mat.Sci.
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Purdue University
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