AIP | Applied Physics Letters

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Citation: Applied Physics Letters **73**, 1284 (1998); doi: 10.1063/1.122150
View online: http://dx.doi.org/10.1063/1.122150
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/73/9?ver=pdfcov
Published by the AIP Publishing

Structured luminescent porous silicon layers produced with laser assisted chemical etching

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(Received 20 March 1998; accepted for publication 2 July 1998)

An approach to the problem of preparation of laterally structured luminescent porous silicon is proposed. The effect is based on the photosensitivity of chemical etching of silicon. Contrary to the other technique recently reported where the porous layer was modified with laser assisted dissolution, a one stage fast anodization-free process is used. Any desired 2D microstructure can be produced, depending on the illumination pattern, which is defined by optical imaging. The accuracy of the method as well as morphology and the luminescent properties of the prepared layers are studied. © *1998 American Institute of Physics.* [S0003-6951(98)04135-7]

The discovery of efficient visible electro- and photoluminescence (PL) from porous silicon (PS) in 1990[1] was the first step towards the technology that would allow optical and electronic devices to be integrated on silicon wafers. Anodization in hydrofluoric acid (HF) is usually used for preparation of PS, as electric current is needed to supply holes to the surface being etched.[2] The detachment of one Si atom can be expressed as follows (only surface hydrogen atoms taking part in the reaction are shown):

$$\mathrm{Si}_n\mathrm{H}_2+4\mathrm{F}^-+2\mathrm{H}^++2h^+\rightarrow\mathrm{Si}_{n-1}\mathrm{H}_2+\mathrm{SiF}_4+\mathrm{H}_2\uparrow,$$

where holes help to substitute fluoride for hydrogen on the passivated Si surface. However, intense illumination is capable of generating enough electron-hole pairs for the etching to occur.[3] Contrary to the case of using electric current through the solution, spatial control of illumination is possible, enabling us to define the lateral structure of PS.

Etching occurs only if the wafer is *n* type, which supports the assumed mechanism of the process where holes are driven to the surface by the Schottky barrier between the wafer and the solution. 10 Ω cm *n*-type Si(111) wafers were used in our work. Less resistive wafers are etched easier but give no luminescence. According to a simple depletion approximation, the thickness x_0 of the barrier can be estimated from the equation

$$x_0=\sqrt{\frac{U\epsilon_0}{2\pi ne}},$$

where U is the height of the barrier and n is the doping concentration. For our samples with $U=0.5$ eV and $n=1021\ \mathrm{m}^{-3}$. This gives a barrier thickness 50–100 nm so that holes are less likely to enter the pore wall when its thickness becomes less then 200 nm and walls are not etched further. With higher concentration of donors, the depletion layer is thinner, it does not fill the core of the wall, and holes penetrate into porous structures which allows further dissolution. Experiments with (100) wafers showed no difference from the (111) wafers in the morphology of the mesoporous structure. Figure 1 shows scanning electron microscope image obtained from the top and edge views of the PS layer produced. The morphology is sponge-like with microscale voids and nanoscale walls. The porous layer is clearly defined from the bulk substrate and its thickness is comparable to the photon absorption length (3–5 μm for the He–Ne laser light).

The porous layer has broadband visible PL centered at 680 nm (Fig. 2). When prepared with blue or green illumination, samples have much thinner porous layers with much weaker PL in the same wavelength region, which could be caused by a short photon absorption depth causing dissolution of the porous layer.

For the first attempt at defining the lateral structure of

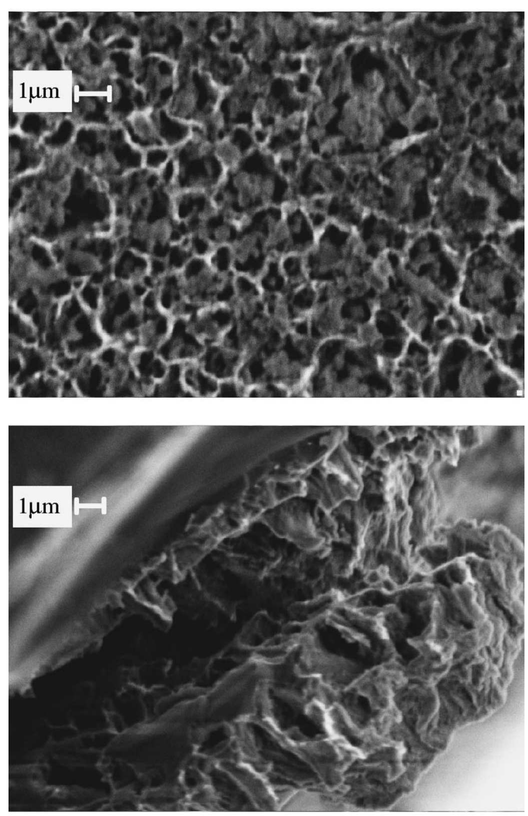

FIG. 1. Scanning electron microscope images of the PS layer prepared with laser assisted etching.

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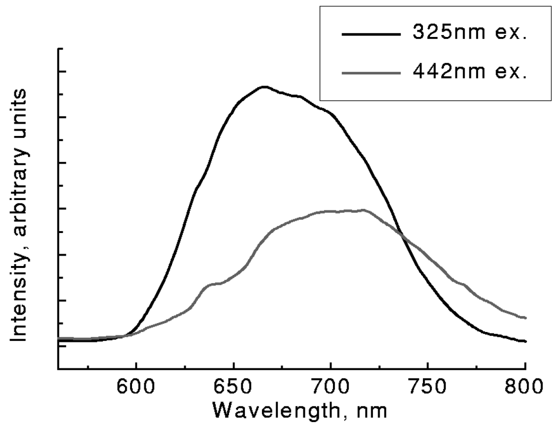

FIG. 2. PL data for PS prepared with laser assisted etching. Spectra for two different excitation wavelengths: 325 (black) and 442 nm (grey) are shown.

the porous layer we projected the reduced image of a 2D copper grid (the sort used in transmission electron microscopy) on the wafer during etching. A 20 μm spaced array of porous regions was produced. Figure 3 shows a typical atomic force microscope image of the sample. 50 wt % HF solution, with a small amount of added ethanol, and low power 633 nm laser light were used. The estimated power density on the sample was around 5 mW/mm^2 taking into account focusing geometry and interfacial reflections. The pattern appears in 2–5 min and the thickness of the porous layer saturates in 10–15 min. Dark porous regions (Fig. 3, main field) correspond to areas illuminated during the etching. Large scale cracks do not appear with shorter etching time but the thickness of the porous layer decreases. To study the interface profile between porous and bulk phases the porous layer was removed with weak KOH solution. This revealed the underlying surface of bulk silicon with the same 2D periodicity and sinusoidal depth profile (Fig. 3, insert).

The quality of the pattern produced is close to the best possible for the present setup if one considers the spherical aberration of the lens used. The longitudinal misfocus δl of the light entering a plano-convex lens at a distance h from the axis can be expressed as

$$\delta l = -\frac{(n-1)h^2}{2R},$$

where R is the radius of curvature and n is the refractive index of the lens. To get a rectangular rather then sinusoidal pattern higher order spatial Fourier harmonics are required to act in image formation. For the lens used a 5 mm aperture h was needed to use one central and four side components of the Fourier image of the grating, which gave 5 μm aberrational feature broadening on the image. Calcium fluoride (CaF_2) components introduced into the optical scheme would allow a short-focus objective to be positioned close to the wafer, which would improve the quality of the image. The accuracy of the process with a single-dot illumination and optimum process parameters were studied in our previous work.[4] Lateral superlattices of smaller size down to one micron were produced recently[5] using an illumination pattern formed as the result of laser interference. Two significant differences between their work and our approach are that here (1) any desired lateral structure can be produced without being limited to periodic patterns, and (2) no preliminary electroetching is used so there is no intermediate porous layer between the structured porous layer and the bulk silicon. On the other hand, with the initial bulk crystalline structure of our sample, carrier diffusion puts more limitation on the resolution of the technique, as the carrier diffusion length in the bulk Si exceeds that in PS by a factor of 20–30.[6] Wafers with more lattice impurities could be used to help recombination, which would reduce minority carrier diffusion.

The quality of the etched profile could also be affected by acoustic vibrations of the solution-to-air interface (the beam enters the solution through the open top surface in our setup). The deviation of the beam from its equilibrium position γ due to an angular perturbation of the surface α is

$$\gamma = \alpha \frac{n-1}{n},$$

where n is the refractivity of the solution. For the 5 mm distance to the sample in the solution, this gives 5 μm loss in the accuracy of the image for 3×10^{-3} rad angular amplitude of surface perturbation. This can be easily avoided if a CaF_2 side window, rather than air-to-liquid interface, is used for beam entry.

The distortion of the image projected to the bulk silicon caused by the light scattering in the porous layer is unlikely to be comparable with the other effects mentioned above. For a rough estimation we can refer to the Mie formula.[7] With a typical wall thickness of 100 nm used for calculation of size parameter, more than half of all 633 nm light is scattered for angles less than 20°. Although our structure can hardly be considered as round spheres, this suggests a negligible distortion of the image when the depth of the porous layer is less than the lateral feature size.

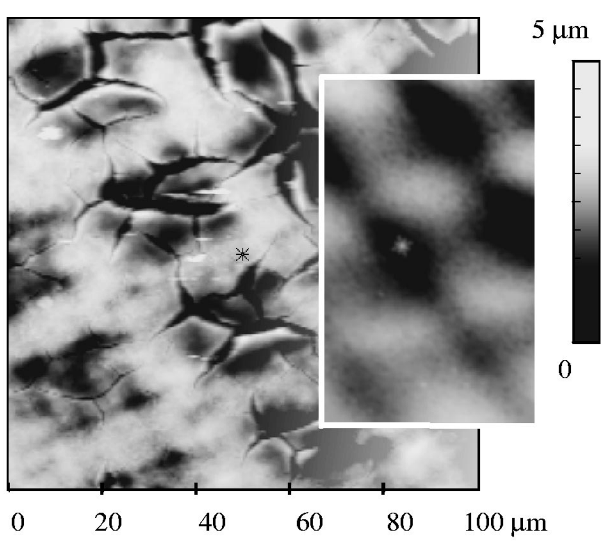

FIG. 3. Structured porous silicon layer and the relief of the underlying bulk silicon (insert) viewed using atomic force microscopy. The grey scale black to white on the image corresponds to a depth difference of approximately 2 μm.

To conclude, a new fast anodization- and mask-free technology for preparation of 2D structured PS layers on bulk Si substrate is demonstrated. The method promises new possibilities for silicon-based optoelectronics, optical data storage, and photonics.

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