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Ultrasound treatment for porous silicon photoluminescence enhancement

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One of the most important properties of the porous silicon is its strong visible photoluminescence. However the intensity and the shape of the photoluminescence is changing as the sample ages, due to absorption of oxygen and hydrogen in the skeleton of the porous layer. This is why a good passivation for the porous silicon is crucial in order to fabricate a stable and reliable device with well-defined characteristics. Porous silicon was exposed to an ultrasonic treatment in order to increase the photoluminescence intensity and to passivate the layer. In this work we show that the ultrasound treatment increases the photoluminescence intensity by a factor of 2–3 in a very short period of time (10 min). Long ultrasound treatment results in a smaller increase of the photoluminescence intensity but dramatically slows the aging process of the porous silicon. We believe that the ultrasonic treatment introduces some energy to the porous silicon, allowing the traps in the skeleton to be repopulated. In this process, the deeper traps get occupied while the shallower traps are kept free, allowing the photoluminescence to increase and the aging process to decay.

1 Introduction Porous silicon (PS) is a subject of intensive research since Canham [1] found its strong visible photoluminescence (PL) in 1990. The research towards a working electronic device based on PS focuses on contacts and passivation for the PS layer. Few passivation techniques have been introduced in the last years including high temperature oxidation [2], NF_3 anealing [3–5] and mechanical coverage for sealing. These passivation techniques are based on the idea of keeping away the contaminants from the dangling bonds in the PS skeleton by means of not exposing the opening bonds to the surrounding gas. We introduce a technique that is based on a new idea of changing the dangling bonds behavior by occupying the deeper traps of the skeleton, and releasing the shallower traps used for the PL intensity and detection functionality. Ultra sound treatment (UST) is known to be a very powerful tool for the defect annealing and dislocation removal, as was demonstrated on poly-silicon [6–7] and on II–VI semiconductors [8]. We applied this technique to PS layer while trying to avoid damaging the fragile structure of the porous structure.

In this work we show the PL intensity for PS samples that were exposed to the ultra sound treatment (UST) as a function of the UST duration and the aging time after the treatment. We also show skeleton images obtained from atomic force microscope (AFM) and scanning electron microscope (SEM).

2 Experimental Large areas (5 cm^2) of porous silicon layer were fabricated on a low conductivity p-type (111) crystalline silicon by applying a 150 mA direct current in electro-chemical cell containing a

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HF: ethanol solution in 1:1 ratio. The current density was 30 mA/cm^2 resulting to a porosity level of 65%. The thickness uniformity of the fabricated PS layer was very high (deviation of less then 5 nm), as was measured by refractive techniques. By varying the time of the etching process, PS layers with various thicknesses were fabricated, corresponding to a rate of 1 μm/min. The different thickness of the PS samples (3, 10, 15 μm) was used to ensure that the thickness of the PS layer had no effect on the results of the UST. The conditions that were applied for the UST were a frequency of 70 KHz, an excitation voltage of 6 V_{p-p} and a current of 2 mA_{p-p} activating the piezoelectric ultrasound transducer. Some samples were aged at room temperature, while others were aged at 170 °C, to accelerate oxidation and aging.

3 Results and discussion The first set of samples was used in the UST time test. In this experiment, we used the measurement setup as shown in Fig. 1, which allowed us to check the PL intensity during the UST. The results of this experiment are shown in Fig. 2a. The second set of samples was used to check the aging of the PS layer after UST. We measured the PL intensity before and after aging, for samples that were exposed to UST and for samples that were not exposed to UST. The PL measurements for those samples are shown in Fig. 2b and Fig. 2c. A third set of samples was used in the accelerated aging at 170 °C, so that we aged two samples, one during UST and the second without UST. The PL intensity of the third set is shown in Fig. 2d.

From the PL measurements in Fig. 2 we can learn few things: Fig. 2a is showing that there is an optimal ultra sound treatment time to achieve maximal PL intensity which is 2.5 times higher than that of the non treated sample. This time is of the order of 10min while a longer UST time results in a decrease of the PL intensity. So, the final improvement in the PL intensity is about 50%. Fig. 2b shows an aging process non treated samples which causes a typical increase in the PL intensity and a slight blue shift for the PL. Fig. 2c shows that the samples treated by UST exhibit a stable PL behavior even after aging process (two months). This stabilization has been achieved after UST of 180 min, and the PL has not been changed after this time. Fig. 2d shows the samples that were aged at 170 °C for 10 min, which accelerates the aging process. One can see that samples that were not treated by UST during the aging

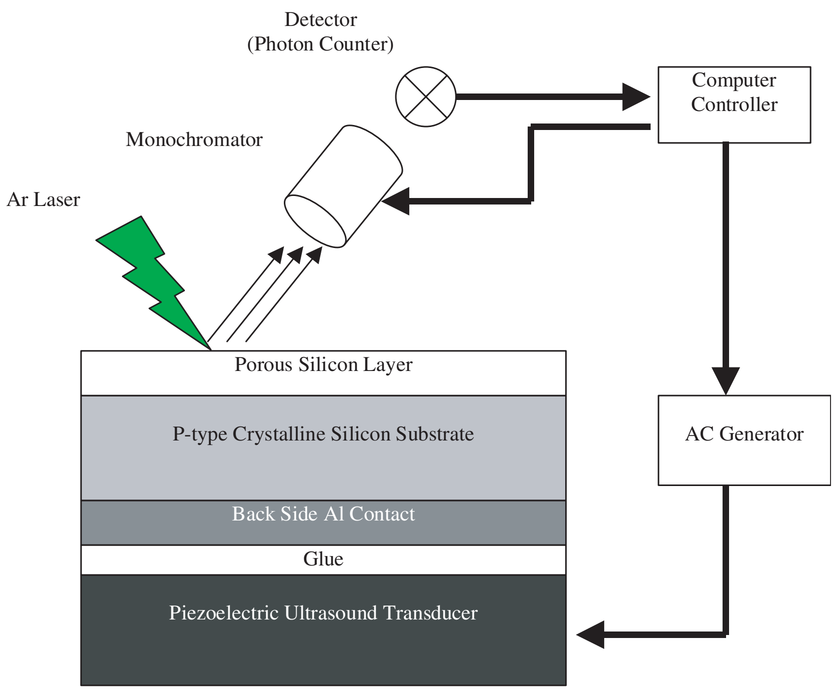

Fig. 1 (online colour at: www.interscience.wiley.com) Ultrasound treatment measurement setup.

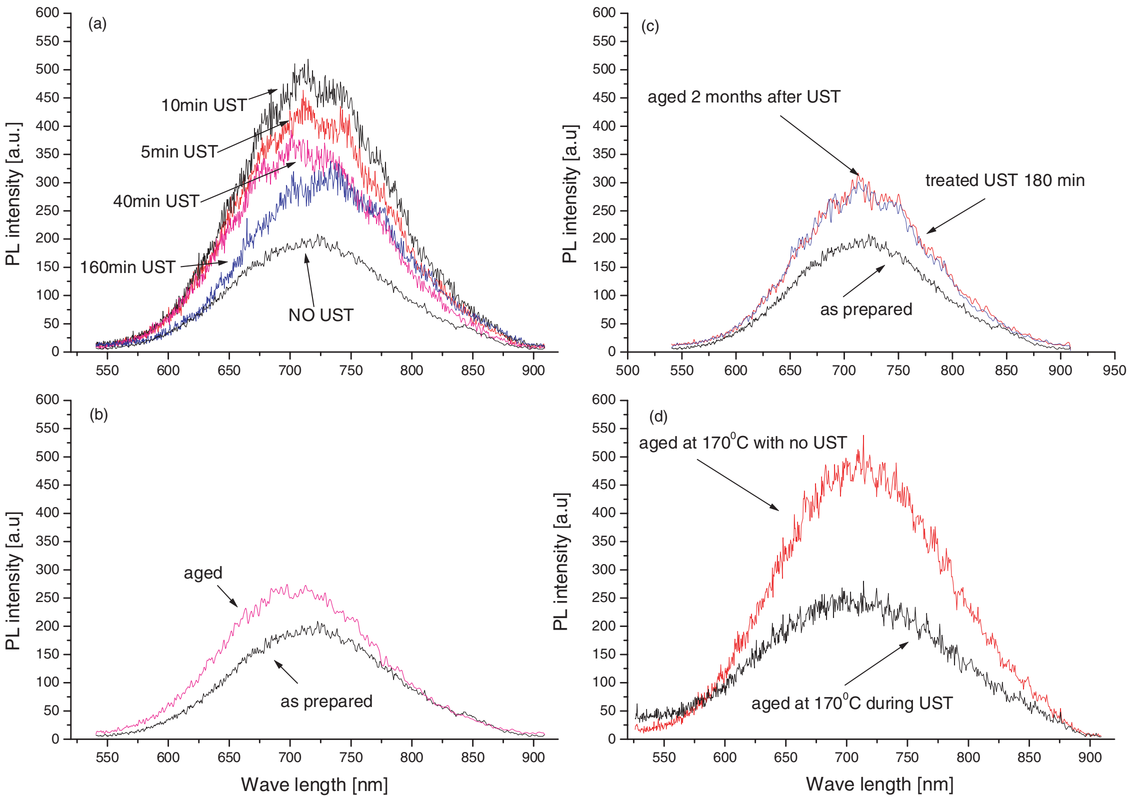

Fig. 2 (online colour at: www.interscience.wiley.com) Photoluminescence measurements a) as a function of the ultrasound treatment duration for as prepared PS, b) PS aged at room temperature with no UST, c) PS aged at room temperature after UST d) PS aged at 170 °C after UST.

process show a rapid aging behavior, while the samples that were exposed to UST during the aging process show almost the same behavior as those that were aged a long time at room temperature after UST.

In order to ensure that the PS layer skeleton was not mechanically affected by the UST, SEM cross-section images of cleaved samples were taken. AFM images of the samples surface were also recorded. In Fig. 3a–b and Fig. 4a–b we show those images for samples before UST and after 180 min of UST. It is clearly seen from Fig. 3 and Fig. 4 that the mechanical structure of the PS was not affected by the UST. The skeleton and the surface in the SEM images look very similar for the treated and untreated samples.

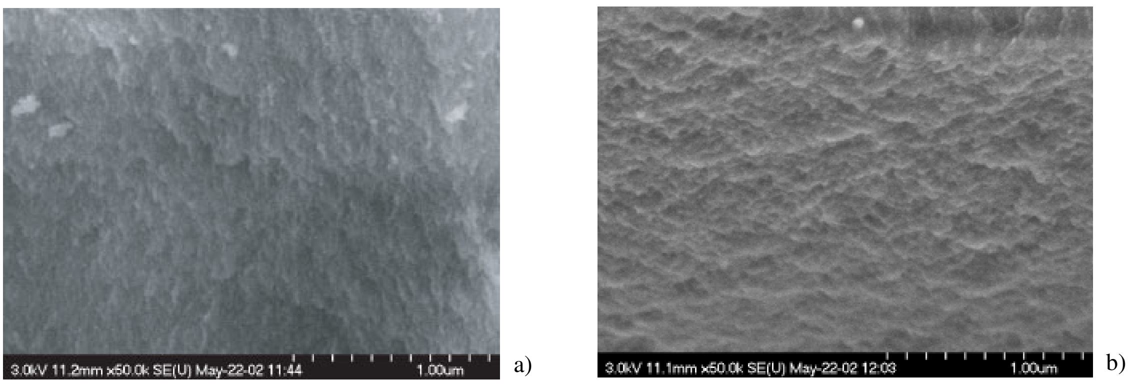

Fig. 3 SEM images of 10 μm PS layer a) before UST b) after UST for 180 min.

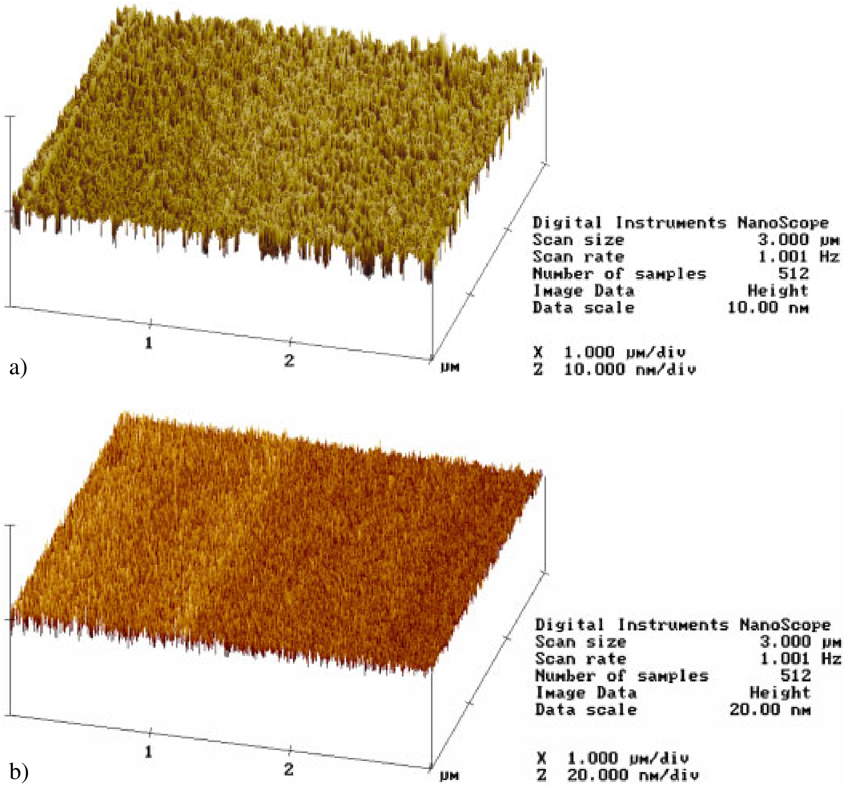

Fig. 4 (online colour at: www.interscience.wiley.com) AFM images of 10 µm PS layer a) before UST, b) after UST for 180 min.

We believe that the UST introduces a large amount of energy to the porous silicon structure. This energy is small enough in the mechanical scale, so that mechanical damages are not introduced to the PS skeleton. On the other hand, this energy can, and probably does, repopulate the dangling bonds of silicon atoms. Since aging is a process that populates dangling bonds in the porous silicon skeleton, the ultra sound treatment is a competing process to the aging. The repopulation process is build from two competing processes, releasing atoms from the shallow traps, and populating deeper traps by adding energy to skeleton, helping it to absorb atoms or reconstruct the silicon bonds at the surface. Like any complex processes, there is a time when a maximal efficiency is achieved. At this time we expect the photoluminescence to reach a maximal value, as can be observed in the PL measurements in Fig. 2a. For example, at the beginning of the UST the PS dangling bonds can be cleaned from the various absorbed contaminations, leading to increase of the PL intensity. The cleaned surface of the PS gets reconstructed via UST resulting in stabilization of the PL properties.

The process of populating the deeper traps in the skeleton stops the aging almost completely as observed in Fig. 2c. The stabilization of luminescence properties of PS is the most important effect achieved by the UST. The short (few minutes) UST repopulates some of the dandling bounds, so that the PL increases (similar to aging), but the short UST does not completely stabilize the skeleton, so that the aging process can still affect it.

4 Summary In this work we show that the ultrasound treatment increases the photoluminescence intensity by a factor of 2–3 in a very short period of time (10 min). Long ultrasound treatment results in a smaller increase of the photoluminescence intensity but dramatically slows the aging process of the porous silicon. Thus, ultra sound treatment results in both improvement and stabilization of the porous silicon luminescence properties.

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