



## Full Length Article

## Decalin-assisted light emitting porous Si formation and its optical, surface and morphological properties

Ali Karatutlu<sup>a,b,\*</sup>, Sumeyra Istengir<sup>c</sup>, Sedat Cosgun<sup>d</sup>, Isa Seker<sup>e</sup>, Bayram Unal<sup>f</sup><sup>a</sup> Centre for Condensed Matter and Materials Physics, School of Physics and Astronomy, Queen Mary, University of London, London, E1 4NS, United Kingdom<sup>b</sup> Electrical and Electronic Engineering, Bursa Orhangazi University, YILDIRIM/Bursa, 16310, Turkey<sup>c</sup> Physics Department, Yildiz Technical University, Yildiz Teknik Üniv., Beşiktaş/Istanbul, 34349, Turkey<sup>d</sup> Bionanotechnology RD Centre, Fatih University, Buyukcekmece, Istanbul, 34500, Turkey<sup>e</sup> Department of Medical Services and Techniques, Fatih University, Buyukcekmece, Istanbul, 34500, Turkey<sup>f</sup> Computer Engineering, Istanbul Sabahattin Zaim University, Küçükçekmece/Istanbul, 34303, Turkey

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## ABSTRACT

In this research paper, light emitting porous silicon (Lep-Si) samples were fabricated by a surfactant-mediated chemical stain etching solution in order to form homogenous luminescent nanostructures at room temperature. As an industrially important solvent, decalin (decahydronaphtalene) was used as a surfactant in the HF/HNO<sub>3</sub> solutions in order to control the etching process. Morphological, surface and optical properties of the Lep-Si samples were examined using atomic force microscopy, X-ray photoelectron spectroscopy, photoluminescence (PL) spectroscopy, and laser scanning confocal microscopy (LSCM) techniques. These characterization techniques were correlated with the various etching times including depth dependent luminescence profiles for the first time. We report the optimum conditions for production of the most efficient Lep-Si using decalin (decahydronaphtalene) and possible structural origins of light emission using the depth dependent luminescence measurements.

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## 1. Introduction

Si in bulk form is a poor light emitting material due to its indirect band gap [1]. The discovery of the luminescent porous silicon [2,3] at room temperature has prompted many research groups [4–15] to investigate a variety of methods to produce light emitting porous silicon (Lep-Si) specimens for various applications. Lep-Si samples have found numerous applications including LEDs [11], solar cells [16–19], sensors [20–22] and hydrogen production [23]. Lep-Si can be produced by submerging a Si wafer into HF/HNO<sub>3</sub> solutions. The ultimate aim of an etching solution is to control several parameters including porosity, pore size, thickness [24].

Still there are some complications in order to fully control the stain etching solution for formation of uniform pores on the sample surface. Surface active agents (surfactants) offer an opportunity to reduce surface tension and improve wetting between the wafer surface and the aqueous solution and thus formation of homogeneous nanostructures [25,26]. This can then lead to control and design

to change size, thickness and morphology of the pores of Lep-Si. In this study, we report for the first time an electroless etching solution using an industrial solvent, decalin (decahydronaphtalene), its optimum conditions for production of Lep-Si and possible structural origins of light emission using the depth-dependent luminescence measurements. We also demonstrate using atomic force microscopy studies that the nanopore surface of the fresh sample was almost fully covered with oxides due to long term exposure to the atmosphere and recovered by a 10 s HF re-treatment.

## 2. Experimental procedure

The crystalline Si (c-Si) wafers utilized were p-type (Boron doped) having (100) orientation, >1 ohm cm resistivity and a thickness of 525 μm. The standard wafer cleaning procedure known as RCA1 [27] was applied to all of the unprocessed Si wafers which were then dried using Ar gas just before the stain etching process. Then, HF acid solution (49 wt.%) / HNO<sub>3</sub> acid solution (69 wt.%) with a respective ratio of 400/1 was applied to the Si wafer for various etching times. The Si wafers were etched during 2 min, 5 min, 7 min, 9 min and 12 min. For possible formation of a homogeneous Lep-Si layer, 1 ml of decalin (decahydronaphtalene), a mixture of cis and trans (reagent grade, 95%) as a surfactant was used

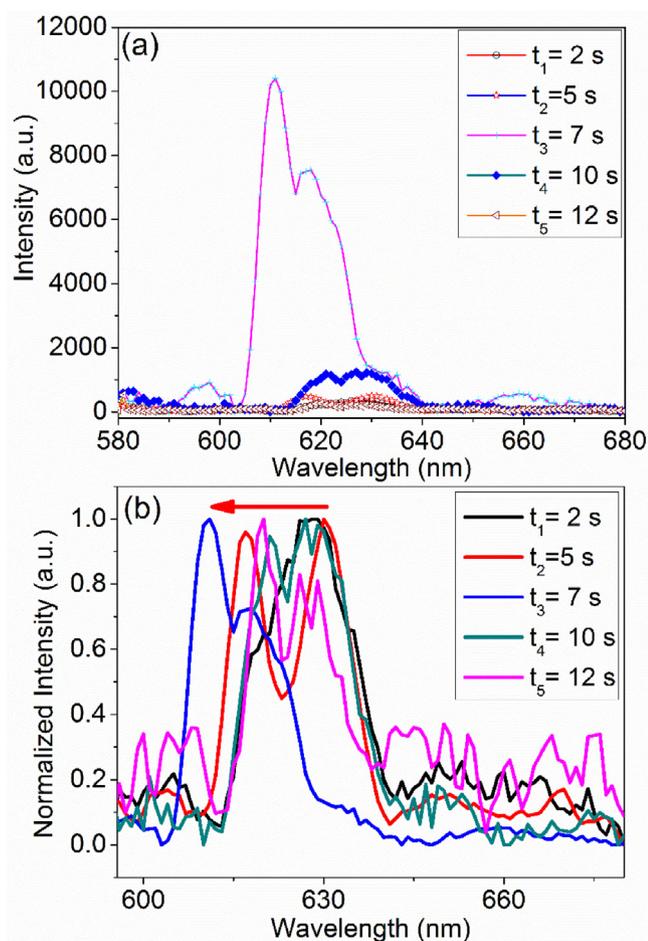
\* Corresponding author at: Electrical and Electronic Engineering, Bursa Orhangazi University, YILDIRIM/Bursa, 16310, Turkey.

E-mail addresses: [ali@alिकaratutlu.com](mailto:ali@alिकaratutlu.com), [a.karatutlu@qmul.ac.uk](mailto:a.karatutlu@qmul.ac.uk) (A. Karatutlu).

as purchased from Sigma-Aldrich. at 25 °C (room temperature) at ambient light. The decalin was released by a micropipettor inside the HF/HNO<sub>3</sub> solution prior to the wafer insertions. The PL spectra were obtained from fresh samples with an assembled UV-PL spectrometry and the fresh samples were referred to the as-prepared samples which were kept in Ar gas flow just after the each etching process and prior to the PL measurements recorded within a collection time of 30 s. The depth-dependence of PL intensity from the fresh Lep-Si samples prepared under the same conditions has been recorded using a laser scanning confocal microscope (LSCM, model no: Leica TCS SPE). The LSCM measurements were taken at 1 μm depth range with the scanning rate of 250 nm/min. The surface study of the Lep-Si prototypes was performed by an X-ray photoelectron spectrometry (XPS). The XPS investigations were carried out using a Kratos 800 spectrometer with an Al K $\alpha$  X-ray source (15 kV, 300 W) under a base pressure of 10<sup>-9</sup> mbar and the take-off angle at 54.7°. All the samples were kept in air for 4 weeks before conducting the XPS measurements including reference c-Si. Atomic force microscopy images were recorded by a Park Systems XE 100 AFM using non-contact mode and analyzed by a software called “XE Image processing program”. We have recorded all the AFM measurements using a silicon tip, radius <10 nm, with an Al coating on its backside.

### 3. Results and discussion

Fig. 1(a) shows the etching time-dependence on the PL spectra of the Lep-Si samples. The normalized PL data also given in



**Fig. 1.** (a) The PL spectra and (b) normalized PL spectra of the Lep-Si samples with increasing the etching time. In the PL measurements, the excitation wavelength of 350 nm was used.

Fig. 1(b) show clearly a blue shift of the peak of the PL spectrum of the Lep-Si sample formed at the end of 7 min etching compared to the PL spectra of others. First of all, we should emphasize that 7 min of etching yields the most efficient PL emission and thus considered to be optimum etching time for formation of nanopores (nanopillars) where excitons (electrons and holes) are considered to be confined. This is due to the fact that chemical etching process results in the subsequent steps of formation of nanopillars and polishing of nanopillars until the Lep-Si sample is removed from the etching solution. The blue shift, on the other, is generally considered to be due to fact that the decrease of nanopillars size in Lep-Si samples would result in a phenomenon, known as quantum size effect (QCE) giving an increase in the HOMO-LUMO gap [28–30]. Furthermore, considering the notion of QCE given in these studies, it can also be considered that the size distribution of the nanopillars of the Lep-Si samples affects the FWHM of the PL peaks [12]. The PL intensity from the Lep-Si samples in this work increases sharply by the etching time until 7 min and then reduces. Based on the Gaussian fit to the PL spectrum, the analysis results in two emission bands at 617 nm (sharp peak) and 621 nm (the shoulder). The trend of comprising two emission bands seems to be consistent for all of the etching times as shown in Fig. 1(b). In addition to the nanopillar size, the PL peak quenching is known to happen by other competing factors including surface termination, the structural modification and existence of disorder. H-termination upon chemical etching was reported by Buriak [25] showing a dependable increase of the H-termination by increasing the etching time in a 10% HF solution for some time (for 2–10 min) and then corresponding stretching IR mode almost vanishes for further exposure (for 15 min) to the HF solution. The H-termination and the dissolution of Si wafer seems to be a successive and continuous process until the complete dissolution or removal of the sample from the solution. The underlying etching mechanism of the HF treatment of a Si wafer is complicated and believed to be not well understood although the etching process is widely used in the field. The authors finds the Si dissolution mechanism proposed by Kolasinski reasonable [31]. His study demonstrates that metal assisted HF etching yielded a H-terminated surface which was found to be stable at least for 30 min.

The depth-dependent integrated PL intensity measurements of the Lep-Si samples were taken using LSCM and are presented in Fig. 2 only for the various etching times under the same etching condition. Their luminescent images using LSCM were also recorded and are given in Fig. 2. Both the PL intensity and the depth-dependent PL intensity were found to be maximum for the sample etched for 7 min (shown as  $t_3$  in Figs. 1 and 2 respectively). The luminescent images provides information about how the PL emission intensity varies all over the Lep-Si samples in XY axes. Capability of recording the luminescent intensity in Z-direction can also shed light on understanding the possible spatial origin of the light emission. For instance, the PL emission of the Lep-Si formed after 7 min of etching time is maximum at the sample surface and fades away quickly once departing from the surface (see  $t_3$  in Fig. 2). However, the spatial origin of PL emission of the Lep-Si sample prepared after 2 min of etching was observed to be nearly at a depth of 2 μm (see  $t_1$  in Fig. 2). Compared to the thickness of the c-Si wafer (525 μm), this depth could be considered to be the surface of the sample. This suggests that the spatial origin of the light emission in Lep-Si sample can be the etching time dependent. The spatial origin in the Lep-Si samples can be precisely considered to be shifted from the core to the surface (from  $t_1$  to  $t_3$  respectively). Two hypotheses for the shift of the spatial origin of the light emission can be considered at this stage. In the first scenario, during 2 min of etching time, nanopillars (and nanopores) could be expected to be formed with the surface H-termination. Then, the dissolution mechanism would be repeated and cause to increase the H-termination on the

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