Synthesis and Characterization of Luminescent Amorphous Porous Silicon (ap-Si) Nanoparticles via unconventional Stain Etching

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Abstract. Starting from crystalline silicon we synthesised bright suspensions of amorphous porous silicon nanoparticles through unconventional stain etching. Upon excitation with UV light, this novel nanostructured material gives rise to an intense red photoluminescence (PL) which resembles that of some silicon nanostructures. We studied the properties of the prepared nanoparticles using a number of cutting-edge characterization techniques such as TEM, SEM and EDX. The complete crystalline-to-amorphous phase transition, confirmed by the morphological studies, seems fortuitous.

1. Introduction
Taking into account its abundance (second most abundant material on earth) and prominence (most widely used semiconductor in electronic and optoelectronic applications) [1-9], silicon in many respects is one of the most important elements in both nature and chemistry. It has however poor optical qualities. The indirect band gap of bulk crystalline silicon used in the semiconductor industry is too low (1.1 eV) to be used in optical applications [10]. Nonetheless, the desire for integration of optoelectronic devices with silicon microelectronics has stimulated an intense effort to search Si-based materials that emit light efficiently [11]. As they approach the nanometer scale, silicon structures, like those of other elements, exhibit unique optical, electronic and physical properties [12-14]. Their properties are interesting from both a fundamental perspective and a practical viewpoint [13]. In the early 1990s, nanostructured silicon, also known as porous silicon (p-Si), was reported to exhibit a surprising visible emission when excited with UV light. Ever since this remarkable discovery by Canham [15], p-Si spurred a great deal of interest among the science community, particularly for its staggering optical properties [15].

Even though the mechanism for its light emission remains rather controversial, fascination towards porous silicon continues to grow. Given its compatibility with the existing electronic platform and their unique optical properties, p-Si has been extensively studied as a promising optoelectronic material and a
more efficient photovoltaic material. Furthermore, the ability to select the emission wavelength i.e. red, green and blue emission, of p-Si by adjusting the erosion process of porous silicon [16-19], is appealing for many applications.

In this work, we will review the fabrication as well as the obtained properties of silicon nanostructures derived from p-Si films via an optimized chemical etching process.

2. Experimental

Because of the air- and moisture-sensitive chemicals, we performed all experiments at room temperature under controlled atmosphere. All sample handling was performed in an argon-filled glovebox (MBraun) to avoid sample contamination and to prevent further oxidation. All chemical reagents were used as received without further purification. For amorphous porous silicon formation, hydrofluoric acid (HF, 49%, Sigma-Aldrich), hydrochloric acid (HCl, 35%, Sigma-Aldrich) and iron (III) chloride (FeCl₃, 98%, Alfa Aeser) were used. Colloidal silicon nanoparticles (SiNPs) were fabricated through electroless stain etching process. Single crystal silicon wafers (boron-doped, (100), 1-10 Ω.cm, Addison electronics) were cleaved into 2.5 x 4.5 cm strips and immersed in a 50:1 solution of deionized water and hydrofluoric acid (49%, Fluka) for 3-4 min for native oxide removal (Scheme 1 *). Cleaned strips were then submerged into an etching solution composed of HF, HCl and FeCl₃, for 13 hours (Scheme 1 **). This solution creates an electroless chemical reaction in which the metal ion oxidant (Fe₃⁺) injects as a hole into the valence band of the silicon atoms, which initiates the reaction and stimulates p-Si formation [20]. The addition of HCl produced much stable and reproducible samples than etchants composed of just Fe₃⁺ and HF. Following etching, wafer strips were washed out through brief dipping in deionized water followed by rinsing in absolute toluene then dried under N₂ stream (Scheme 1 ***). In last, the NPs were dispersed in an organic solvent (toluene, Chromasolv grade, Sigma-Alrich) after breaking-up the formed porous film by sonicating the strips for 45 min.

The surface morphology of ap-Si nanoparticles was investigated by scanning electron microscope (SEM) and transmission electron microscopy (TEM). SEM was performed in an FEI Nova Nano-SEM 50, at voltage 2 keV. TEM were recorded using FEI Krios CT-TEM at an operating voltage of 120 kV. Fluorescence spectra were obtained using a Horiba Fluoromax-4 spectro-fluorometer. Absorbance measurements were carried out using a Genysis 10S UV-Vis spectrometer (Thermos-Scientific). We conducted Brunauer-Emmet-Teller (BET) porosimetry measurements to measure the surface area and pore size distributions of the samples, using an ASAP 2420 area and porosimetry system (Micrometrics). Composite homogeneity of the optimized stain etching procedure as well as the chemical analysis of the
produced nanoparticles were investigated by energy dispersive X-ray spectroscopy (EDX) in conjunction with SEM. All characterization measurements were performed under standard conditions while maintaining low air exposure.

3. Results and Discussion

A wide spectrum of synthesis methods have been developed for the fabrication of nanostructured silicon. These include chemical stain etching, chemical vapor etching, laser-induced etching, and metal-assisted etching as well as spark processing and reactive ion etching. Each method could produce a nanostructure of specific features [21-25]. Normally anodic etching and stain etching are the most used techniques [26-27]. The setup and the process of anodic etching are however complex and expensive. Meanwhile, stain etching is rapid, simple, and cost-effective with large product yield [28-31].

In this work, starting from p-type crystalline silicon wafers, we used electroless colloidal stain etching (Scheme 2) to synthesize bright red-emitting suspensions of colloidal amorphous porous silicon nanoparticles. This etching process yielded a highly luminescent porous silicon film with a unique dual layer structure.

Scheme 2. An illustration of stain etching process using FeCl₃: (a) HF etching removes chemically oxidized layer and leave the surface H-terminated, (b) generation of the holes generated during the reduction reaction, (c) electron removal from nearby Si-H bonds, (d) activation of Si-H passivated bonds, (d) etching resulted in the formation of SiF₆²⁻, and (e) evolution of porous film of amorphous nanostructured silicon.

The morphology of the etched silicon surface was examined by SEM. The interaction between the sample and the impinging electron beam provides insight into the morphology, topography, and composition. Fig. 1 shows that the surface of the etched film is covered with nodules of 10 μm in diameter and 6 μm in height with a gap between them and the bottom surface (shown in Fig. 2). The upper and
lower interfaces of the 6 μm thick film were flat and well-defined in shape. The top portion of the film is mainly composed of nodules while the bottom layer consists of a film that seemed to be more adherent to the substrate; moreover, the thermos-capillary forces cracked and partially exfoliated the top layer of the film (see Fig. 2).

Figure 1. SEM micrographs of the (a) top view of the surface, and the (b) blow-up of the top surface of an etched silicon substrate.

Figure 2. Cross-sectional SEM image for the produced film of p-Si. The exfoliated region exceeded 2μm in thickness whereas the lower layer remained intact and exceeded 6 μm in thickness.

TEM studies carried out on the surface of etched silicon showed that the films are typically characterized by a graded transition from bulk to a shallow high porosity region. It is clear that the surface of the etched silicon becomes porous (see Fig. 3). TEM micrographs, depicted in Fig. 3, confirm that the
laterally etched film (stain film) consists of two layers: a fragmented coarse-grained upper layer exhibiting a very high porosity that looks like a damaged surface layer. Whereas the bottom layer shows flat fine uniform texture (Fig. 3c). The film mostly composed of a homogenous distribution of pores. We suggest that the upper layer of the film is mechanically less stable because it has higher porosity than the bottom layer. Diffraction patterns (inset of Fig. 3c) obtained from both films showed them to be amorphous. (The diffraction spots are blurred because the size of the coherent region is smaller compared to single crystal silicon.)

![Figure 3](image)

**Figure 3.** TEM micrographs of porous silicon film etched for 13 hours. (a) The upper and lower interfaces were both sharp. (b) The top layer exfoliated and separated from the bottom part along an irregular crack. (c) TEM image of amorphous porous silicon NPs. FFT pattern is shown in the inset.

The uniform flat films of etched substrates (strips) demonstrated a shiny appearance (Fig. 4b) under UV illumination, before being dried under N₂ stream. During drying the films took on a rough golden brown appearance as seen in Fig. 4c. Such a color change indicates the portion in which the stain etched film is formed, where surface discoloration occurred. The upper portion of the film appeared brighter, indicating a higher degree of charging because of its higher porosity.

![Figure 4](image)

**Figure 4.** Surface of cleaved silicon strips under UV illumination (a) before etching, (b) after texturing through stain etching and before sonication, and (c) after drying and sonicating the textured strips.
Sonicating the stain etched strips removed the nodules from the surface layer as a consequence of the mechanical interaction of sonication-generated cavitation bubbles with the porous surface layer. The suspended particles were in the order of 10 \( \mu m \) in size as shown in Fig. 5. Fig. 5b shows that the amorphous porous silicon nanoparticles exhibited a cauliflower structure of hundred nanometers in size. These particles were further milled through additional sonication step. Ultracentrifugation was used to remove the clusters that are larger in size, and that would not remain suspended.

![Figure 5](image)

**Figure 5.** (a) SEM micrograph of FeCl3-assisted etched ap-Si nanoparticles after sonication, and (b) a high magnification SEM image of one nodule.

To quantitatively determine the surface area of our ap-Si NPs, a BET porosimetry measurement were conducted. BET indicated that the ap-Si nanoparticles have a surface area of ~ 300 m\(^2\) g\(^{-1}\), with an average pore size of 3.5 nm. This large amount of surface area may be the driving force behind the crystalline-to-amorphous phase transition during the etching process [32]. Gravimetric analysis of the synthesized ap-Si NPs revealed that the average yield was approximately 0.4 mg of ap-Si per cm\(^2\) of the silicon wafer or 10 mg per 10 ml of the solvent (toluene). Dispersing nanoparticles in a non-polar organic medium, such as toluene, is a major challenge as the particles tend to aggregate easily. Toluene, however, does not contain any oxygen that could react with the sample and was therefore used as a dispersing medium to avoid further oxidation.

TEM investigation showed the presence of roughly spherical particles (Fig. 6), which tend to aggregate during preparation of samples for TEM. High-resolution TEM together with the corresponding fast Fourier diffractogram (FFT) of the processed nanoparticles revealed no indication of crystallinity in these nanospheres. They are completely amorphous, and the absence of lattice plane fringes in the former, and the broad diffuse ring in the latter are characteristic signatures of amorphous structures.
Figure 6. (a) A high-resolution TEM image of the processed ap-Si NPs, and (b) a higher magnification image. The inset is the corresponding diffraction pattern obtained by Fourier transformation showing amorphous structure.

We have performed EDX measurements in conjunction with SEM to analyze the chemical composition of this novel nanostructured material. The result of this study is presented in Fig. 7. From the spectra, it can be seen that silicon is clearly the dominant element in the powder. The small trace of oxygen is attributed to air exposure during sample transport as silicon is readily oxidized. The Cu peak is arising from cupper-made sample holder.

Figure 7. EDX spectrum of amorphous porous silicon nanoparticles.
Fabricated ap-Si nanoparticles exhibited a bright orange-yellow color under white light. This is also considered as an indication of lack of crystallinity, as crystalline silicon has a metallic luster with a grayish color. Qualitatively amorphous porous silicon samples, prepared under sonication, displayed a more uniform luminescence and less pitted porous silicon surface to the naked eye than non-sonicated samples. Fig. 8 shows the UV-Vis absorbance, PL excitation, and PL emission spectra of ap-Si NPs. Our samples exhibit strong UV-Vis absorbance at wavelengths below 400 nm.

![Figure 8. UV-Vis Absorbance (blue), PL excitation (red), and PL emission (black) spectra of ap-Si nanoparticles dispersed in toluene.](image)

The recorded photoluminescence spectra exhibited an excitation peak at 350 nm while the emission peak was centered at 600 nm. It is worth mentioning that while the upper layer is fragile, its PL is not, even after being removed from the substrate. Moreover, samples made up of toluene and kept under N₂ atmosphere were able to maintain their emission for more than one month.

Nevertheless, the etched film and the sonicated one not only exhibited different structures, but they also had different PL behavior [33, 34], as shown in Fig. 9. The shift in PL peak position is mainly due to the difference in the porosity of the top and bottom layers. It could also be a result of interactions between the porous silicon layers and the bulk silicon underneath. It is remarkable that the colloidal nanostructures in the suspension, regardless of their size, produce homogeneous emission.
Figure 9. PL emission spectra of ap-Si etched film (black curve peaking at 638 nm) and the underlying substrate from which they were extracted (red curve peaking at 620 nm). The ultra-bright PL emission, seen in and measured for the suspension of amorphous porous nanostructured silicon, renders it an interesting material to study.

4. Conclusion
In conclusion, we succeeded in obtaining high visible photoluminescence from originally non-luminescent crystalline silicon via unconventional stain etching method. This was attained by developing new formulations of stain etchants inducing rapid, efficient and scalable process to fabricate amorphous porous silicon nanoparticles with widely reproducible outcomes. The high visible photoluminescence of the treated nanoparticles is attributed to porosity, and the particular property might be useful for the realization of light-emitting silicon-based optoelectronic devices. The peculiar hollow structure of the ap-Si nanoparticles could also be useful for trapping or storing molecules. It is important to note the passivity of the produced ap-Si nanoparticles as demonstrated by the EDX spectrum, which indicates that the pristine film contained nothing but hydrogen-terminated silicon elements. These colloidal nanostructures can be used in many applications, such as liquid LEDs, liquid filters [35] and solar energy harvesting [1] as well as oxygen detection in solution and on surfaces.

5. References
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