Influence of the fabrication process on the light emission of Macroporous Silicon

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ABSTRACT

Macroporous silicon structures have been fabricated by electrochemical etching. Such fabrication process is known to result in the presence of a thin microporous Si layer at the walls of the macropores and at the surface. Photoluminescence measurements conducted in plan-view and cross-section exhibit a wide emission peak around 650nm which can be attributed to the microporous Si. The combination of a photonic crystal and a light emitter in one structure represents a potential for applications that has not been studied previously. This preliminary study shows the influence of the main fabrication parameters, namely the current density and the etchant solution, on the emission properties of the microporous Si layer.

Keywords: emission, macroporous Si, microporous Si, photonic crystal

1. INTRODUCTION

Macroporous silicon structures have been extensively studied recently due to their interesting optical properties as photonic crystals [1-5]. The interest of these structures lies in their capabilities of controlling the emission and the propagation of light waves as well as the prospects of inhibited spontaneous emission and opens the door to their potential applications in optoelectronics, information processing and biosensing [6-12].

One way to fabricate two-dimensional photonic crystals in Si is by electrochemical etching in hydrofluoric acid [1-8]. Such fabrication process is known to result in the presence of a thin microporous Si layer at the walls of the macropores and at the surface [1,3,5,6]. Generally, this microporous layer is disposed off by a simple post-fabrication process. However, it is important to notice that the microporous silicon structure itself presents very interesting optical properties. A significant blue shift of the absorption edge and visible room temperature photoluminescence are attributed to the existence of a porous sponge-like silicon skeleton with dimensions of a few nanometres [13-17]. By adjusting the formation conditions, the dimensions of the porous Si skeleton can be increased by several orders of magnitude and its optical properties tuned [13,14,18,19].

The combination of a photonic crystal and a light emitter in one structure represents a potential for applications that has not been studied previously. We present here the first steps of this study by investigating the influence of the main fabrication parameters, namely the current density and the etchant solution, on the emission properties of the microporous Si layer. Photoluminescence measurements conducted in plan-view and cross-section exhibit a wide emission peak around 650nm which can be attributed to the microporous Si.
2. METHODOLOGY

The details of the electrochemical pore formation process have been the subject of many papers in the last decade or so [1-8]. In n-type silicon substrates with [100] orientation, macropores with typical diameters of 20 μm down to 2 μm and a depth of up to the wafer thickness can be formed (fig. 1 shows an example of an ordered macroporous Si structure). To achieve this, the wafer is anodized in an aqueous hydrofluoric acid (HF) electrolyte and the backside of the wafer is illuminated e.g. by a tungsten lamp. If this process is applied to a polished Si wafer, the macropores will grow in a random pattern. To build ordered macropores, one can use standard lithography and subsequent alkaline etching to generate an ordered array of etch pits. The pore formation will then start at these pits and regular pores arranged in well-defined arrangements can be fabricated.

We used n-type [100] float-zone (FZ) silicon with 1–2 Ω cm resistivity. First, the wafers were pre-structured by oxidation, standard lithography and subsequent tetramethyl ammonium hydroxide (TMAH) etching in order to form the initial pits. The photolithographic mask used provides a triangular arrangement of holes with center-to-center distance of 5 μm. Then, indium tin oxide (ITO) was sputtered on the backside of the wafers to provide a low-resistance transparent ohmic contact. The wafer (as a working electrode), with counter and reference electrodes, was incorporated in a custom-built electrochemical etching cell. The electrochemical cell is part of a specialized in-house constructed etching rig that also comprises a computer regulated backside illumination and a heat exchanger with thermostat for temperature control, and can be seen in figure 2.

Figure 1: SEM photo of a typical ordered Si macroporous structure.

Figure 2: Photo of the electrochemical cell setup made in-house.
The wafers were anodized in 2.5 wt.% aqueous hydrofluoric acid (HF) with the pre-structured front side in contact to the electrolyte. The wafer backside was illuminated by a 100 W halogen lamp, coupled to an IR cut-off filter to prevent hole generation near the surface. The applied voltage was measured in relation to the reference electrode positioned close (5 mm) to the wafer. Upon removal from the etching reactor, the wafers were rinsed in deionized water and dried in N$_2$ stream. Table 1 summarises the etching conditions for the samples studied in this work. Such conditions have been chosen in order to study the influence of the process temperature and etchant solution, on the emission properties of porous silicon. The experiments were carried out at room temperature (RT) of about 20°C, except sample C which was etched at 10°C.

Table 1: fabrication parameters for the samples studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>current density, J, mA/cm$^2$</th>
<th>Voltage, V</th>
<th>Electrolyte</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (1528)</td>
<td>4.7</td>
<td>1.2</td>
<td>2.5 wt.% aqueous HF</td>
<td>20</td>
</tr>
<tr>
<td>B (1552)</td>
<td>4.7</td>
<td>1.2</td>
<td>2.5 wt.% aqueous HF with Triton-X100 surfactant (about 0.39 mM)</td>
<td>20</td>
</tr>
<tr>
<td>C (1553)</td>
<td>2.9</td>
<td>1.2</td>
<td>2.5 wt.% aqueous HF</td>
<td>10</td>
</tr>
</tbody>
</table>

In order to obtain pores with the same diameter in all samples, the current density was optimised as follows: The obtained pore diameter is a function of the etching current density. For our triangular pattern, the porosity $p$ of the sample and hence, the pore diameter $d$ can be calculated through:

$$p = \frac{\pi}{2\sqrt{3}} \left( \frac{d}{a} \right)^2 = \frac{J}{J_{ps}}$$  \hspace{1cm} (1)

where $a$ is the pitch of the triangular pattern; $J$ and $J_{ps}$ are the applied and critical current densities, respectively. The critical current density $J_{ps}$ is a function of temperature [20] and therefore different current densities were used for the samples etched at different temperatures in order to obtain a porosity $p=0.3$ in all cases.

After cleaving, the etched samples were examined on a JEOL JSM6400 scanning electron microscope (SEM). Photoluminescence (PL) measurements were carried out using an epifluorescence setup (schematic shown in fig.3) from an Olympus Microscope (model BX51M). Filters were used so as to select the (480–500) nm wavelength region of the spectra of a tungsten white light source as the excitation source and so as to collect emission signal above 500nm. The collection of the emission was done through an objective with 150X magnification, then into an optical fiber connected to a spectrometer (OCEAN OPTICS) onto a CCD camera, connected to a computer. The PL measurements were conducted in both cross-section and plan-view. In the plan-view configuration, the excitation light comes perpendicular to the surface of the sample. For the measurements in the cross-section configuration, the samples were actually cleaved and the excitation light came at a right angle to the length of the macropores, exposing the microporous Si layers. This configuration enables to avoid the surface contribution to the PL signal and therefore the signal detected is directly and solely correlated to the emission of the microporous layer situated inside the pores (the entrance of the tubes is not taken into the field of the objective for the measurements, only part of the tubes are studied, as can be seen in photos 5a and 5c). For taking the digital photos of the various sections of the macroporous Si, the samples were illuminated by a white light source and a CCD camera (Q-Imaging) equipped with a colour filter replaced the detection system.
3. DATA

Macroporous Si was optically characterised by room temperature photoluminescence. Both cross-section and planar configuration were looked at to be able to obtain information on the state of the surface of the structure (planar case) as well as on the inside of the pores (cross section case). To start with, figure 4a shows the PL spectra taken in both configurations, from samples prepared at room temperature. The plan-section measurements (curve i) in fig. 4a) exhibit an emission peak around 660nm. Now, looking at the measurements conducted in cross-section, the same emission peak can be observed with slightly decreased intensity. Finally, although not shown here, the same sample was subsequently post-etched, and the previously visible PL signal disappeared.

A variation of the fabrication conditions was conducted to see its influence on the emission of the macroporous Si structure being under investigation here. Sample C was fabricated at lower temperature and therefore at lower current density (see table 1). Looking at the PL spectra of this sample in fig. 4b in the cross-section configuration, two effects can be seen: an increase in intensity (by a factor of 2.5) and a red-shift of the PL emission (in the order of 15 nm). Such effects can also be seen for the signal obtained in the planar configuration (although not shown here). An effect of this fabrication condition can also be seen in the SEM photos shown in fig. 4. Photo 4a represents the sample A, made under normal conditions. In the macropores wall, a darker layer can be detected, considered to be the thin microporous layer present in the pores. Such layer can be seen a lot clearer, due to its width increase in the case of the sample C.
Finally, we will discuss here the effect of the use of surfactant in the fabrication process. Recently, it has been shown that using surfactants instead of ethanol, it is possible to similarly reduce the surface tension and furthermore prevent variation of solution composition with temperature as well as aging [6,21]. Looking at the PL in figure 4b of the third sample fabricated using such a solution, in the cross section configuration, it can be seen that no signal is being detected. PL measurements carried out in plan-section agree well with the cross-section measurements as no signal can be detected (data not shown). The SEM micrograph in figure 6.c also clearly shows the macropores without the presence of the thin dark layer referred to previously as the microporous layer.
From the results of the optical characterisation performed on the macroporous Si, the presence of microporous Si in the structure can be ascertained. The origin of the PL signal observed around 600nm both in surface and cross section configuration can be attributed to the presence of microporous Si. In the plan section configuration, it is the microporous present at the surface of the wafer which is responsible for the PL. The surface microporous Si results from the electrochemical etching process during the fabrication of the macropores. Indeed, microporous Si is standardly fabricated by electrochemical etching and is known to emit between 600 nm and 900nm depending on its porosity [13-17], which in turn depends on the fabrication parameters [15-17]. In the case of the cross-section configuration, the contribution of the surface does not play a role, it can therefore be concluded that in this situation the origin of the PL can be related to the presence of microporous Si on the walls of the (macro)pores. Furthermore, the SEM micrograph in figure 5a clearly shows the presence of a thin microporous Si layer of about 200 nm on the macropore walls. Finally, the post-etching performed on the same sample is known to remove the microporous Si layer [21]. The SEM micrographs showed no microporous Si layer and the corresponding PL signal disappeared. These results agree well with the assumption that the PL signal observed previously had its origin in the microporous Si layer.

It is worth noticing that the digital micrographs of the first macropore structure studied (not shown here) features an interesting detail: the macropores are actually coloured in a pale blue tone when light is shone upon them. This effect can be simply explained by the fact that the presence of a microporous layer results in interferences from the
incident light due to the difference of refractive indexes between air and porous Si [22]. In the case of planar porous Si layers [22], the analysis of such interference pattern conveys information such as the porosity and the layer thickness. In the case of macroporous Si, such information is hard to deduce due to the geometry of the pores, leading to complex interference patterns and colour scheme, and we will not get into such analysis here. In our case, we will just mention that the blue fainted colour indicates a thin microporous layer [22]. The post-etched macroporous Si structure exhibits transparent colourless pores.

A variation of the fabrication conditions was conducted to see its influence on the microporous Si and its emission. In the case of macroporous Si, a very important factor is the current density. The importance of the current density in the macropore fabrication is due to the fact that this process is self-controlled and is determined by the current density $j_{PS}$ through the pores. Sample C was fabricated at lower temperature and therefore at lower current density (see table 1). According to refs. 23, 24 and their SEM and FTIR results, higher current densities result in thinner microporous Si with large porosity. The increase in PL intensity we have observed in our samples processed at lower temperature can be explained by the fact that, although the porosity is lower (therefore a lower emission efficiency and a redshift of the emission), a thicker microporous silicon layer is formed which compensates the loss of emission efficiency previously mentioned. Indeed, it can be observed in the SEM micrographs (fig. 6b) that the lower temperature process does result in a thicker layer of microporous Si on the macropore walls. Roughly, for our sample, a room temperature process results in a microporous Si layer of around 200 nm thickness, while at lower temperature the layer thickness increases up to approximately 500 nm. Finally, it can also be pointed out that the SEM micrographs allow to show that the macropores formed in the two fabrication conditions stated above have the same parameters characteristics (diameter of the pore, length of the pore, etc…). Therefore, this allows to conclude that the change in the PL signal are directly associated to changes to the microporous Si and not to possible changes occurred to the macropores. The optical micrograph of this sample shows a very colourful pattern, with some red and green, which is characteristic of thicker porous Si layers [22].

Generally, the electrochemical etching process produces hydrogen gas and its bubbles block the etchant from the silicon surface [6,25]. The result of this hydrogen production is a partially etched surface. In order to avoid this problem, the addition of ethanol to the HF etchant is commonly used for macroporous silicon formation. Recently, it has been shown that using surfactants instead of ethanol, it is possible to similarly reduce the surface tension and furthermore prevent variation of solution composition with temperature as well as aging [6,25]. Various articles also refer to the use of surfactant in the etching solution as a way to eliminate the microporous Si layer in the walls of the pores [6]. Of course, such effect is dependent on the type of surfactant (anionic or cationic) used and on its concentration (the threshold concentration is referred to as the critical micellar concentration CMC) [6]. In the case of Triton X (non ionic surfactant), the CMC is roughly about 0.22 mM and the concentration we have been using is about 0.39 mM. The PL signal in both planar- and cross-section configurations has disappeared. This infers that the microporous Si present at the surface of the wafer has equally been removed as the microporous Si layer present at the walls of the pores, as expected. The SEM micrograph in figure 6.c also clearly shows the macropores without the presence of a microporous layer in the walls.

5. CONCLUSION

In this paper, we have shown that the microporous Si layer present at the surface and at the walls of the pores in a macroporous Si structure emits visible light. We have investigated the changes in the microporous Si layer characteristics as a function of fabrication parameters by photoluminescence and SEM analysis. Such results correspond to the first step into investigating the potential combination that represents the macroporous Si structure: a photonic crystal and an efficient emitter, both being the result of the same fabrication process. Such study is important for potential use of the macroporous/microporous Si structure towards applications.
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