Study of p-type Porous Silicon

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Abstract— Porous silicon fabricated by electrochemical etching was studied using Scanning Electron Microscope and Elemental Differential X ray Analyzer. The etched samples were found to emit red luminescence when exposed to ultraviolet light of wavelength 254 nm. Micrographs of the samples obtained by Scanning Electron Microscope showed a porous layer at the surface. Elemental Differential X ray Analysis provided the evidence of oxidation of a porous layer. Red luminescence emitted from the surface may be attributed to confinement of holes in the oxidized layer.

1. INTRODUCTION

Porous silicon (PS) has received considerable attention due to its photo- and electro-luminescence emission in the visible range. Surface-pore morphology of etched silicon plays an important role in emission process [1], which is controlled by parameters governing the etching reaction [2, 3]. A shift in the photoluminescence spectra to longer or shorter wavelength also depends upon etching conditions [4–6]. Though a lot of work has been done on porous silicon yet a comprehensive picture to understand the mechanism that produces luminescence in the visible range is still not clear [3]. Surface reaction follows different paths under different etching conditions. In an earlier study [1], Fluorine concentration (Si-F) was found on the etched surface after a reaction with concentrated HF. In another report by R. L. Smith et al. [2], HF treated silicon surface showed a high concentration of hydride species with a predominance of monohydride on the etched surface. Such discrepancies suggest that more work is required to understand the role of porous silicon in photo- and electro-luminescence emission [1]. We report here a study on oxidized surface of HF-pretreated silicon using Scanning Electron Microscope (SEM) and Elemental Differential X ray Analyzer (EDX).

2. EXPERIMENTAL

One side polished p-type silicon wafers have been used in electrochemical etching. 1–20 Ω cm resistive wafers were grown along (100)-direction by Czochralski (CZ) technique. 40% HF and 95% ethanol solution (1 : 1 by volume) was used as an electrolyte. Sample and platinum wire, 0.5 cm apart, were used as an anode and cathode, respectively. Approximately, 80% area of the samples ($50 \times 30\,\mathrm{mm}^2$) was immersed into the electrolyte. A constant current of $32\,\mathrm{mA/cm}^2$ was maintained for two hours across the electrodes. Etching setup is shown in Fig. 1.

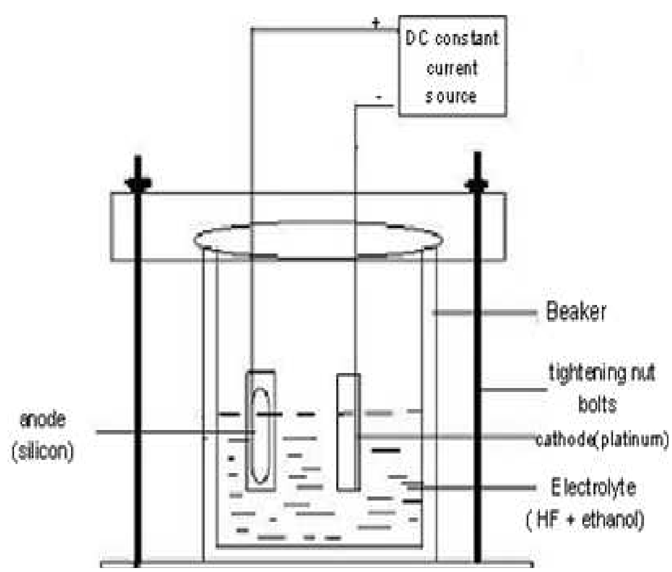

Figure 1: Anodic etching setup.

3. MEASUREMENTS

Immediately after anodic etching, the samples were taken out from the solution and rinsed with de-ionized water and then dried in laboratory air. Samples were exposed to 254 nm ultraviolet (UV) light, red luminescence was found to emit from selective parts of the samples, but within ~ 24 hours the luminescence intensity increased to maximum and whole etched part of the wafer started to emit red luminescence. Further characterization of the as-grown (named A) and etched (named B) samples was carried out using Scanning Electron Microscope (SEM), model JSM-5910 JEOL and Elemental Differential X ray Analyzer (EDX), model INCA 200. SEM micrographs, taken at 500 and 1000 magnification with 20 kV accelerating voltage, are shown in Fig. 2, respectively.

SEM micrographs (a) and (b) of as-grown samples taken at 500 and 1000 magnification, respectively, depict a regular arrangement of rectangle-like grains (high lighted in the figure) with sharp boundaries. Dimensions of grains are roughly less than 10 μm. After etching, micrographs (c) and (d) recorded at 500 and 1000 magnifications are shown in Fig. 2. Porous layer, formed on the surface can be seen in the images. Etching appears to proceed in all direction around the

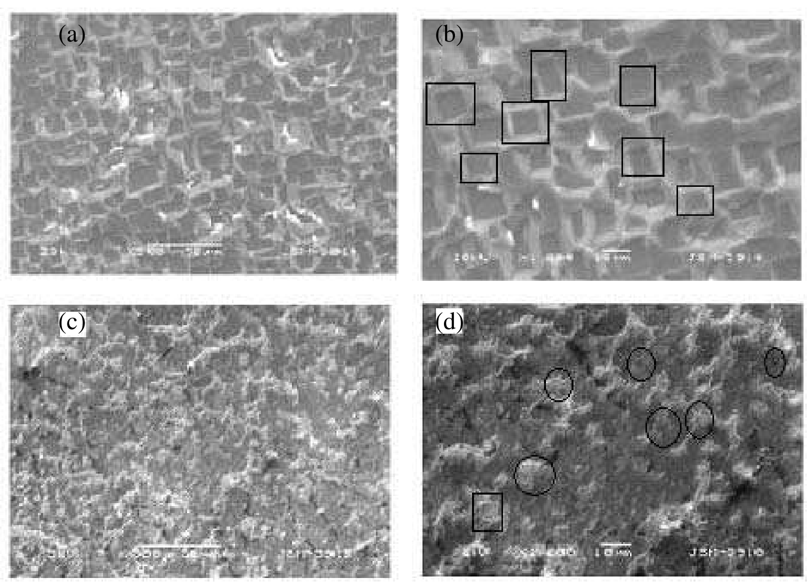

Figure 2: Micrographs of reference and etched samples.

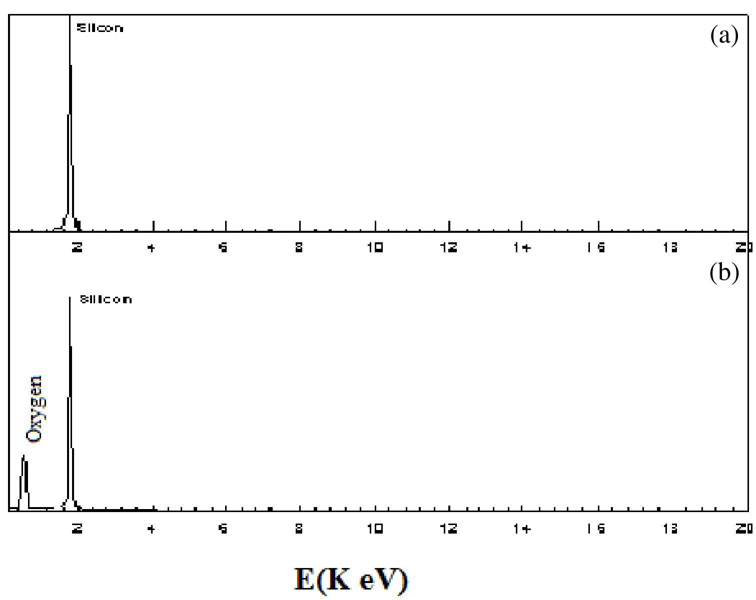

Figure 3: EDX spectra for (a) as-grown (b) etched, samples.

first attacking point, following channel like paths in different directions, as shown by circles in the Fig. (d). Etching on some places proceeds to follow screw like paths as highlighted with a rectangle. After etching grain boundaries disappeared and a new morphology, full of pores, appeared on the surface. Samples were stored in laboratory air. It is noted that luminescence increases with the passage of time, may be due to oxidation. Elemental analyses of the samples have been performed with Elemental Differential X ray Analyzer to check the formation of porous layer on the surface of etched surface. EDX measurements of the samples A and B are shown in Figs. 3(a) and (b), respectively.

Only a single peak corresponding to pure silicon is seen in the spectrum (a). The scan clearly indicates that sample A is 100% pure silicon because no trace of any other element has been found. On the other hand EDX spectrum of etched sample B, shown in Fig. 3(b), reveals an additional small peak along with large peak of silicon. Presence of small peak clearly indicates the formation of oxidized layer.

Weight and atomic percentages of elements measured by EDX are given in Table 1.

Table 1: Weight and atomic percentage of oxygen and silicon in etched samples.

Elements	weight %	Atomic %
Oxygen	27	40
Silicon	73	60

4. RESULTS AND DISCUSSION

The scanning electron micrograph (a) of Fig. 1, recorded at 500 magnification for as grown sample (A) shows a uniformly distributed regular pattern of rectangular shaped grains of (100) silicon. In the Fig. (a), grain boundaries clearly reflect the orientation of the crystal. The same observation is demonstrated in Fig. (b) taken at 1000 magnification. The scanning electron micrograph of etched sample, B, obtained at 500 magnification is shown in Fig. 2 (c). This micrograph shows that regular pattern of rectangular shaped grains has vanished away and instead a porous growth appeared on the surface. The same surface has also been examined using 1000 magnifications, as shown in Fig. 2(d). In both, (c) and (d), figures micro pours are found to distribute uniformly all over the surface.

Weight and Atomic percentage of oxygen and silicon, measured by Elemental Differential X-ray Analyzer (EDX), given in Table 1, indicate the oxidation of the surface in air after etching. Several studies [6–9] have been performed to understand the reaction of silicon surface pretreated in a concentrated HF solution. It was found that fluorine is rapidly replaced by oxygen containing species, when such surface after rinsing with water is placed in air. The exchange reaction is shown by the following equation [1],

$$\text{Si-F} + H_2O \rightarrow \text{Si-OH} + \text{HF}$$

It is thought that OH-group on the surface become polarized and destabilized the Si-Si bonding. The weakened bond is attached with polar H_2O molecule making possible for oxygen atom to form Si-O-Si bonding. Since the Si-O bond in silica has some ionic character [1], oxygen insertion gives rise to a positive charge on an adjacent Si surface atom there by facilitating OH^- to attack on that Si atom followed by oxidation of the Si-H bond. The remaining Si-O-Si bonds can be oxidized in a similar fashion. It is clear that Si-O-Si group dominates on the etched surface and Si-H group eliminates with time. It can be assumed that in the beginning, immediately after taking out the sample from the cell, other species like hydrides, fluorides and hydroxides are present on the surface, disappear with time and oxidation of the surface increases.

Our results obtained from scanning electron microscope and Elemental Differential X-ray Analyzer (EDX) gives the direct evidence of growth of oxide at the surface of silicon. The porous oxidized surface appears to be responsible for the emission of red color when illuminated by Ultra Violet light. Kebbi et al. [8] and Aria et al. [9] pointed out that passivated surface and quantum confinement of charge carriers are responsible for red luminescence. We propose that oxidized layer of the pores or quantum dots formed on the surface due to etching is of the order of nm or comparable to Bohr radius. This very thin layer of atomic dimension is assumed to be responsible for quantum confinement.

5. CONCLUSIONS

Investigation of the etched silicon has been carried out by SEM and EDX. Oxidized porous layer was found on the surface of etched silicon. Hole confinement of oxidized surface of pores was assumed to be responsible for red luminescence.

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