

Proton beam writing in silicon

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Abstract. Proton beam writing has been used to pattern *p*-type silicon prior to electrochemical etching in hydrofluoric acid. The ion beam selectively damages the silicon lattice, resulting in an increase in the local resistivity of the irradiated regions. This damage acts to slow down the rate of porous silicon formation and modify the properties of porous silicon. The photoluminescence intensity of the irradiated regions is found to increase with proton irradiation into a 0.02 $\Omega\cdot\text{cm}$ resistivity *p*-type silicon. In fact, the intensity increases as the fluence increases from 5×10^{14} to 5×10^{15} protons/cm². By immersing the etched sample into potassium hydroxide, the porous silicon is removed to reveal the underlying three-dimensional structure of the patterned area. As the layer of porous silicon layer becomes thinner with increasing fluence, the remaining structure will have a taller feature height. This technique allows the production of a structure with multiple heights by varying the fluence of the beam.

1. Introduction

Proton beam writing is a lithographic technique which utilizes energetic proton beams, for the fabrication high aspect-ratio, three-dimensional (3D) structures in polymers [1,2]. Such capability is attributed to the long penetration depth and low lateral spreading of MeV protons in materials.

Polesello *et.al.* [3] demonstrated, for the first time, that silicon can be patterned like a resist material using proton beam writing. The proton beam selectively damages the semiconductor lattice, and this acts as an electrical barrier during subsequent formation of porous silicon (PoSi) by electrochemical etching in hydrofluoric acid. This enables local modification and control of the properties of porous silicon formed by ion irradiation, resulting in patterned porous silicon.

In order to incorporate PoSi-based light emitters into a standard optical/microelectronic circuit, it is important to be able to pattern PoSi with sufficiently high spatial resolution. There are many ways of producing patterned PoSi, with photolithography being the most common approach [4]. Fluorescent images have been produced in n- and p-type silicon by projecting a black and white image onto the surface during etching [5]. There have also been many previous ion beam irradiation studies on the production of PoSi. Most of the irradiation with heavy ions showed that light emission is preferentially quenched at the irradiated regions [6]. However, when low fluences are used, the intensity is not completely quenched and a red-shift in wavelength is observed [7]. In this work, 2 MeV protons are used to create patterned areas of light emitting porous silicon.

If the etched sample is immersed in potassium hydroxide, the unirradiated regions are preferentially removed, leaving behind a copy of the patterned area as 3D structure. Various complex structures such as multi-level structures and high aspect-ratio pillars are produced using this technique.

2. Experimental procedures

This process uses the nuclear microprobe facility at the National University of Singapore, which can focus MeV ion beams to spot sizes of less than 50 nm [1]. A focused 2 MeV proton beam is scanned over the silicon surface. As the ion penetrates the semiconductor, it loses energy and comes to rest at a well-defined range of about 48 μm in silicon. Silicon vacancies are created along the ion path, with most of the damage produced at the end of range. According to the stopping and range of ions in matter calculations [8], a fluence of 5×10^{15} protons/ cm^2 , will introduce a defect concentration of $\sim 10^{19}$ vacancies/ cm^3 close to the surface, increasing sharply to a maximum of 10^{20} vacancies/ cm^3 at the end of the range [Fig. 1a]. Under anodic bias, the high density of proton-induced defects effectively traps or recombines with the migrating holes. The resistivity of the irradiated regions is expected to increase by 3-4 orders of magnitude [9]. This significantly reduces the current flow through the damaged volume to the electrolyte, slowing down the formation of porous silicon in the irradiated regions [Fig. 1b]. A higher fluence at any region produces a higher damage concentration, so by pausing the beam for different times at different locations, any pattern of localized damage can be built up in the material.

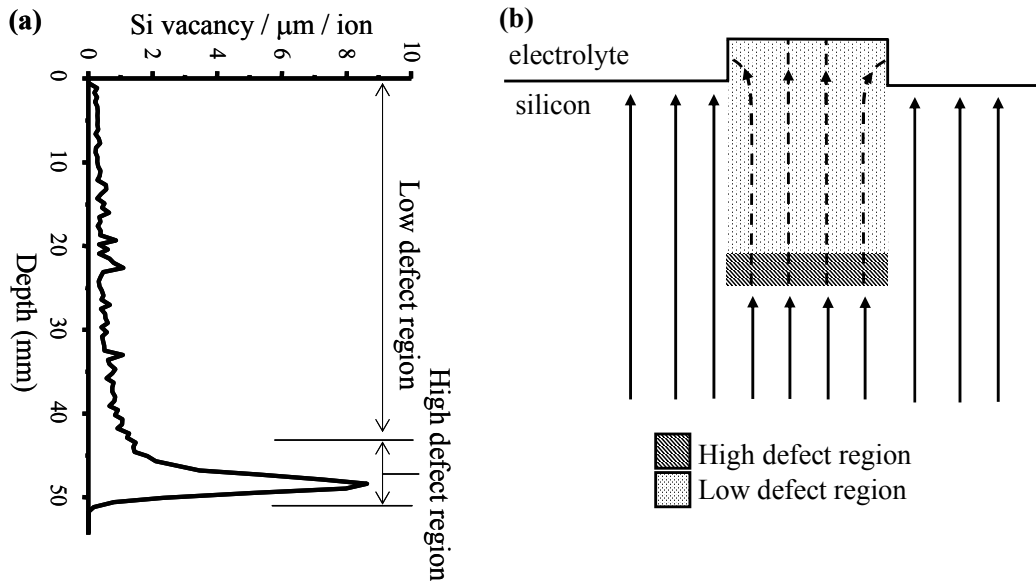


FIG. 1. (a) Vacancy profile of 2 MeV protons in silicon simulated using SRIM [8]. (b) Reduced current flow through the damaged volume during electrochemical etching.

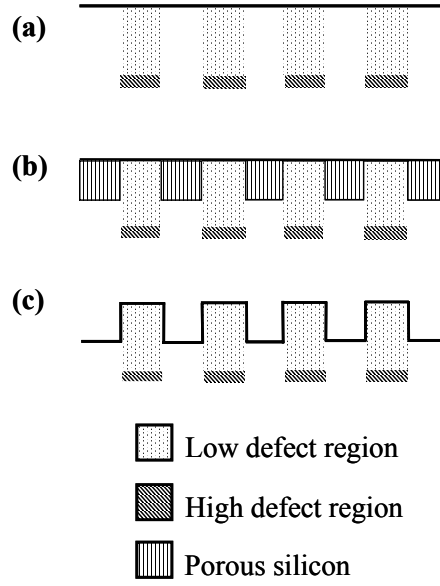


FIG.2. Schematics diagram of the process.

Fig. 2 shows the schematics diagram of patterning porous silicon. Initially, p-type silicon is irradiated using proton beam writing. An electrical contact was made to the back surface using Ga-In eutectic and copper wire. Epoxy was applied to protect the contact from HF. The wafer was then electrochemically etched in an electrolyte mixture of HF: water: ethanol (1:1:2) to produce a layer of patterned porous silicon. Photoluminescence (PL) images of the sample were taken with a CCD camera, excited by a UV lamp through a 395nm long pass filter.

The etched sample is further immersed in diluted KOH for 2-4 min to remove the porous silicon [Fig. 2c] and the underlying structures are then analyzed using scanning electron microscopy (SEM).

3. Results

3.1 Patterned Light Emitting Porous Silicon

A circular ring pattern was irradiated into a low resistivity material of $0.02 \Omega \cdot \text{cm}$ with a fluence of 2.5×10^{15} protons/cm² and then etched at 37 mA/cm^2 for 5 min. Higher PL emission is observed from the irradiated ring pattern, as compared to the unirradiated surrounding regions [Fig. 3]. In earlier studies carried out by Gaburro *et al.*[10], it is shown that the PL intensity depends strongly on the resistivity of p-type silicon. Much higher PL emission was observed on samples with resistivity of $1\text{-}10 \Omega \cdot \text{cm}$ compared to $0.01 \Omega \cdot \text{cm}$. The higher resistivity caused by the damage of the proton beam could have explained the enhanced emission from the irradiated regions.

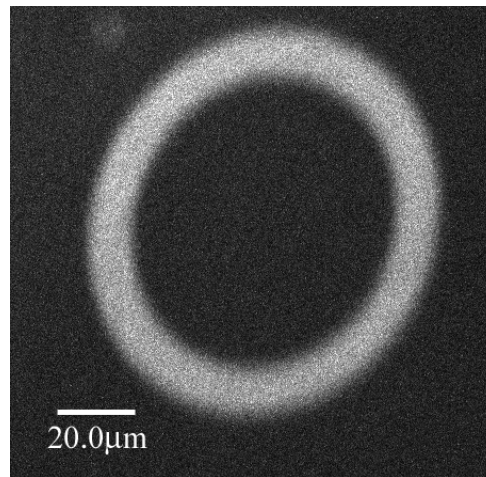


FIG.3. Ring pattern irradiated using proton beam writing.

By increasing the fluence, the local resistivity can be varied to obtain different PL intensity on a single substrate. Fig. 4 shows the optical and PL image of three fringe patterns irradiated with a fluence of 5×10^{15} , 2.5×10^{15} and 5×10^{14} protons/cm². It is shown clearly that the intensity increases with fluence, enabling the intensity to be tuned accurately with the beam.

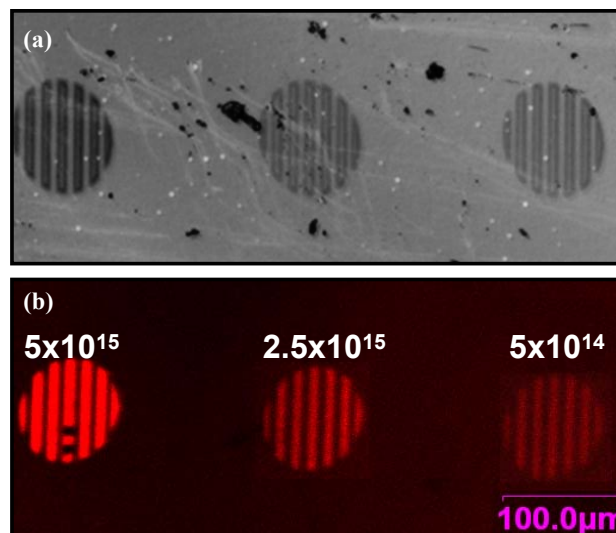


FIG. 4. (a) Optical image and (b) PL image of 3 fringe patterns irradiated with increasing fluence of 2 MeV protons.

3.2 Silicon Microfabrication

The removal of the layer of PoSi reveals the underlying 3D structure of the irradiated patterns. As the rate of PoSi formation slows down with increasing damage, the layer of the PoSi gets thinner, resulting in a higher structure height. Fig. 5 shows the close-up SEM of the irradiated

patterns in Fig. 4 with the PoSi removed. It is shown that the structure irradiated with the highest fluence is taller than that of the lower fluences. This mechanism can be used to produce structures with varying heights or multi-level structures in a single irradiation step.

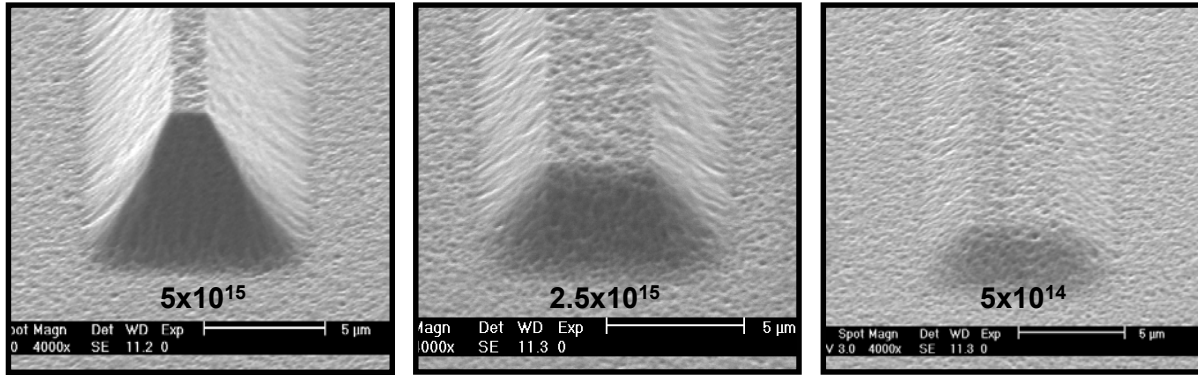


FIG. 5. SEM of the irradiated patterns in FIG.4 with the PoSi removed.

An array of single spots is irradiated into a *p*-type silicon of 4 $\Omega\cdot\text{cm}$ with a fluence of 5×10^{16} protons/ cm^2 . The sample was then etched for 15 minutes with a current density of 37 mA/cm^2 . Fig. 6a shows the SEM image of the uniform array of high aspect-ratio pillars separated at a distance of 5 μm . Each pillar is 6.8 μm high with a diameter of 0.6 μm , as seen from the cross sectional image [Fig. 6b]. The profile of the pillar reveals vertical and smooth sidewalls with slight broadening at the base. As the separation between the pillars reduces to 2 μm , the base of the pillars starts to widen [Fig 7a]. The pillars are joined together at a periodicity of 1.2 μm . This effect can be explained by the lateral spreading of 2.5 μm at the end of range for the 2 MeV protons at the end of range. The current flow between the pillars is significantly reduced as the end of range overlaps, resulting in a much slower rate of PoSi formation in these regions. This places a limitation to the density of structures that can be fabricated.

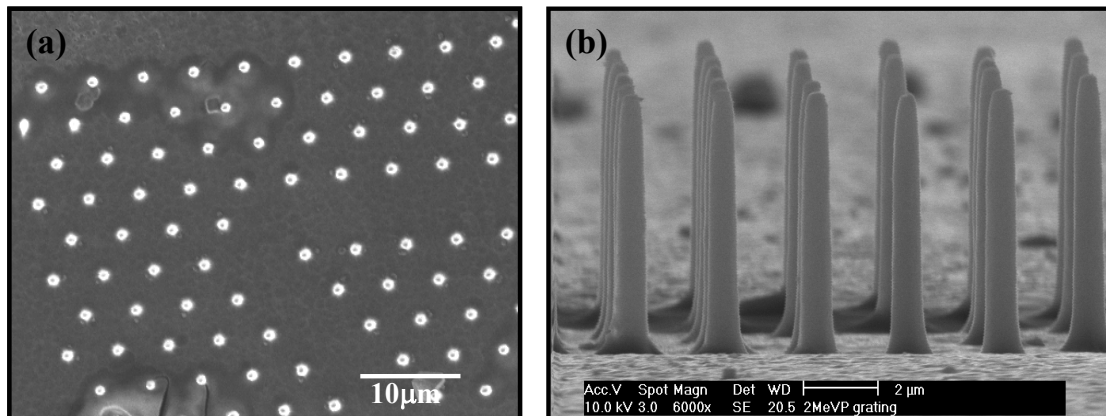


FIG. 6. (a) Top view and (b) cross sectional view of an array of silicon pillars formed by single spot irradiations.

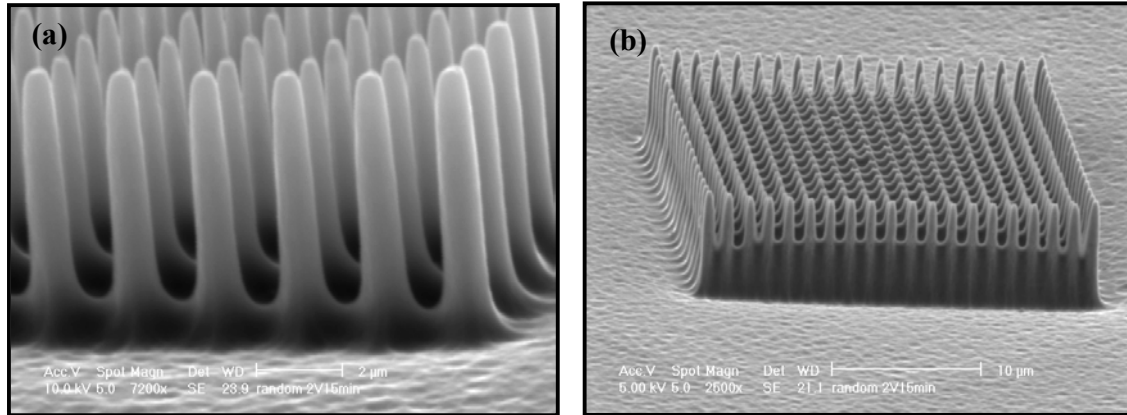


FIG. 7. Array of silicon pillars separated at a periodicity of (a) 2 μm and (b) 1.2 μm .

4. Conclusions

In conclusion, we demonstrated the ability to use proton beam writing for fabrication of patterned light emitting PoSi. Regions irradiated with the proton beam shows enhanced light emission for a low resistivity p-type silicon. This can be attributed to the higher local resistivity created by the ion irradiation. In fact, the intensity of PL emission is shown to increase with the fluence of the beam. By removing the PoSi layer, it is possible to obtain the 3D structure whereby the feature height is increased with higher dose. This provides an effective way of producing multi-level structure without the many processing steps of depositing and removing mask when conventional optical lithography is used. High aspect ratio pillars have also been obtained by single spot irradiations into 4 $\Omega\cdot\text{cm}$ resistivity silicon.

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