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Proton beam writing of microstructures in silicon

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Abstract

The ability to directly pattern the surface of semiconductor wafers using very accurately controlled fluences of finely focused high-energy ion beams has opened up new research directions for the fabrication of a variety of high-aspect ratio, multi-level microstructures in silicon. A beam of hydrogen or helium ions, focused to 50–100 nm in a nuclear microprobe, is used to selectively damage the semiconductor lattice in the irradiated regions. A higher beam fluence at any region produces a higher damage concentration, so by pausing the focused beam for different times at different locations, any pattern of localized damage can be built up in the material. This damage acts as an electrical barrier during subsequent formation of porous silicon by electrochemical etching. This enables local modification and control of the properties of the porous silicon formed by ion irradiation, resulting in patterned porous silicon. If the etched sample is immersed in potassium hydroxide, the unirradiated regions are preferentially removed, leaving a copy of the patterned area as a micromachined three-dimensional structure. The fundamental mechanisms involved in the creation of such porous and silicon microstructures are discussed here.

1. Introduction

1.1. Micromachining

Many new technologies, for example microelectromechanical systems [1–3] and photonic crystals [4], require the fabrication of precise three-dimensional structures in silicon. One major limitation of conventional lithography and silicon etching technologies for these applications is the multiple processing steps involved in fabricating free-standing multilevel structures. Electrochemical etching of silicon in hydrofluoric acid is emerging as an alternative technique for micromachining due to its low cost, fast etching process and easy implementation. Porous silicon is often used as a sacrificial material to fabricate cavities or free-standing structures since it can be easily removed by immersion in a

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potassium hydroxide (KOH) solution. Selective patterning of porous silicon can be achieved through a mask or by etch stop techniques [5]. One drawback of using a mask is that the isotropic nature of the electrochemical etching process results in undercutting of the mask [6].

Recently, Polesello et al. [7] demonstrated the possibility of patterning silicon as a resist material with MeV protons. We have extended this to the micro-fabrication of 3D multilevel structures in silicon [8–10], using the nuclear microprobe facility at the National University of Singapore, which can focus MeV ion beams to spot sizes of less than 50 nm [11,12].

Fig. 1 shows the basis of this method. A finely focused beam of MeV ions is scanned over the wafer surface. The ion beam loses energy as it penetrates the semiconductor and comes to rest at a well-defined range, equal to 8 μm for 2 MeV helium ions, and ~50 μm for 2 MeV protons in silicon. The stopping process causes the silicon crystal to be damaged, by producing additional vacancies in the semiconductor. Most of the beam damage is produced close to the end-of-range, effectively forming localized regions of higher vacancy concentration. A higher beam fluence at any region produces a higher vacancy concentration, so by pausing the focused beam for different amounts of time at different locations, we can build up any pattern of localized damage in the semiconductor material. The irradiated wafer is then electrochemically etched in a dilute solution of hydrogen fluoride. An electrical current is passed through the wafer which causes the formation of porous silicon at the surface [13]. The buried regions of high vacancy concentration inhibit this formation process, so a thinner layer of porous silicon is produced at the irradiated regions. After etching, the porous silicon is removed by immersion in KOH, leaving the final patterned structure on the wafer surface as a three-dimensional representation of the scanned pattern area and fluence. If the etched sample is not immersed in KOH, the porous silicon layer is not removed so the sample comprises patterned areas of porous silicon which may emit light with greater or lesser intensity, or different wavelength, compared with the surrounding unirradiated regions.

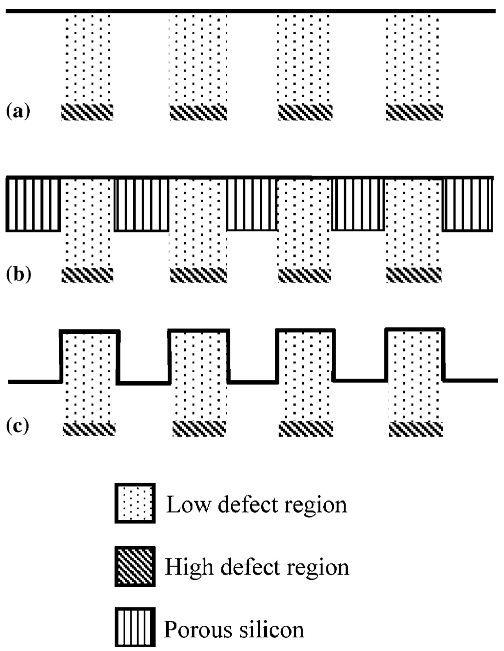

Fig. 1. (a) Patterning of p-type silicon with proton beam writing, (b) electrochemical etching to selectively form patterned porous silicon and (c) removal of porous silicon with dilute KOH solution to form a micromachined structure.

1.2. Patterned porous silicon

Porous silicon (PSi) is of interest due to its photoluminescence (PL) and electroluminescence properties [13–16], raising the possibility of producing light emitting devices made of PSi and microelectronics compatibility [17]. Two distinct visible PL emission bands have been reported from PSi, with different origins ascribed to each. The commonly observed red/orange "slow emission" luminescence band is centred around 1.4–1.9 eV (600–800 nm), and is probably due to quantum confinement effects produced by the low dimensionality of the silicon skeleton remaining after anodisation. After suitable further anodisation the band centre can be blue-shifted to shorter visible wavelengths [18]. The other, higher-energy blue luminescence band is centred at 3.0 eV (~400 nm), and is thought to be oxide-related [19, 20].

A potentially important application of PSi is the production of combined optical/electronic devices incorporating patterned porous material directly onto a single-crystal Si substrate with a high spatial resolution. There are several routes by which patterned PSi has been produced, with photolithography being the most common approach [21]. Fluorescent images have been produced in n- and p-type silicon by projecting a black and white image onto the surface during etching [22]. Variations of the photocurrent produced a shift in the emission wavelength maximum between 640 and 710 nm, and a minimum line separation of 20 μm. Laser irradiation [23] provides a means of varying the crystallite size by photochemical etching, and electron beam lithography has been used to fabricate patterned PSi as a substrate for polymer patterning [24].

Ion beam irradiation of silicon results in lattice defects which locally reduce the concentration of free charge carriers and increase the wafer resistivity [25]. During subsequent electrochemical etching the current flow of holes to the wafer surface and thus the etching rate are reduced compared to unirradiated areas. There have been several previous ion beam irradiation studies on the production of PSi. A fluence of $5 \times 10^{14}/cm^2$ 24 MeV Cl ions was used to quench the PL of 1 Ω cm p-type porous silicon [26]. A fluence of $2 \times 10^{15}/cm^2$ 100 keV Si ions was used to pattern a 3–5 Ω cm p-type silicon through an Al mask [27]. The amorphised, irradiated areas did not produce PL, and a patterned line width of 2 μm was demonstrated. A fluence of 10^{14}–$10^{15}/cm^2$ 30 keV Ga ions was used to pattern n- and p-type silicon using stain-etching, with a resolution of 0.5 μm [28]. Schmuki et al. [29] used a fluence of $3 \times 10^{14}/cm^2$ Si ions to pattern n-type silicon, and showed that the resultant lattice damage produced areas where the pore formation occurred at a lower applied bias than at the unirradiated areas. PL images were created with line widths of 300 nm by careful choice of the bias voltage. A fluence of $10^{16}/cm^2$ 50 keV hydrogen ions was recently used to produce patterned PSi, by irradiating 1–2 Ω cm p-type silicon through a silicon dioxide mask [30]. The measured resistivity of the irradiated areas increased by more than five orders of magnitude. Pavesi et al. [31] used an unfocused beam of 300 keV Si ions with fluences 3×10^{12} to $3 \times 10^{13}/cm^2$ to irradiate 2 Ω cm p-type silicon. Unlike previous studies using high-fluence ion irradiations, use of a low fluence did not completely quench the PL from the irradiated areas; instead, a decrease in porosity from 75% to 65%, and a PL red-shift from 750 nm to 850 nm was observed with increasing fluence.

2. Micromachining results

Here we just give a few examples, but many of our recent results on fabricating high-aspect ratio, multilevel structures in silicon have been published in [8–10].

2.1. Multilevel structures

After etching beyond the end of range, the isotropic etching process starts to undercut the irradiated structure, so multilevel structures can be created by exposing the sample with two different proton energies. Since the structure irradiated with lower energy has a shorter range, it will begin to undercut at a shallower etch depth while the structure with higher energy irradiation continues to increase in height. In this way, we can fabricate multi-level free-standing microstructures in a single etch step. To demonstrate this capability, bridge structures were irradiated with 0.5 MeV protons

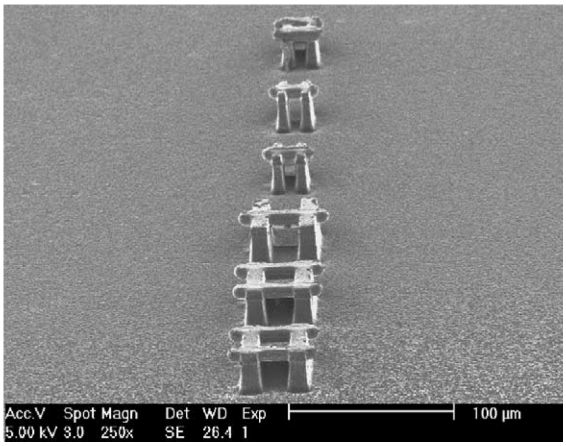

Fig. 2. SEM image of a multi-level micromachined structure.

(range ∼6 μm), and supporting pillars with 2 MeV protons (range ∼48 μm). Fig. 2 shows the resultant structure at an etch depth of 25 μm. The bridges are fully undercut and separated from the substrate. They remain supported by the pillars irradiated by higher energy.

2.2. Non-etching of unirradiated regions

An unexpected effect which can occur in some irradiated, etched structures is discussed here, where unirradiated high-resistivity p-type material is not removed after etching and KOH immersion, as initially assumed.

Fig. 3(a) shows a SEM of a 4 Ω cm p-type wafer in which the outline of a 40 μm × 40 μm square was irradiated using 2 MeV protons. After electrochemical etching and immersion in KOH, the central portion of the square was not removed, even though this area was not irradiated. In Fig. 3(b), a small opening was left in the irradiation of the square outline, resulting in most of the silicon being removed from the central portion except around the opening. In Fig. 3(c), only three sides of the square were irradiated, resulting in complete removal of material from the central region in the final structure.

It may be deduced from Fig. 3 that it is important to consider the geometry of the required irradiated structure in predicting from where silicon will be removed. We are currently investigating this, and similar effects related to the use of focused ion beams for the formation of patterned porous silicon and micromachined structures using the MEDICI code. This models the electrical hole current reaching the surface for a given geometry and fluence of ion induced damage within the silicon lattice. Fig. 4 shows the hole current as a function of lateral distance away from the centre of a 100 μm diameter closed circle, in which the 10 μm thick wall was irradiated with 2 MeV protons. The simulated hole current far away from the structure is large, hence the wafer background will be etched and removed as normal. However, within the closed circle, the hole current is low, hence no etching will occur and no material is removed, in agreement with Fig. 3(a). The reason underlying this effect is electric field lines tend to be excluded from the unetched central region, and are deflected outside the irradiated circle. Such simulations are useful but should not be pushed too far, since they take no account of the time evolution of the electrochemical etching process, or lateral effects arising from conventional chemical etching.

3. Patterned porous silicon results

3.1. Decreased PL intensity from ion irradiated areas

Fig. 5 shows photoluminescence images of two areas of high-resistivity (4 Ω cm) p-type silicon irradiated with different proton fluences. The unirradiated background regions exhibit red/orange PL, with a peak wavelength emission at 640 nm. The darker areas correspond to the

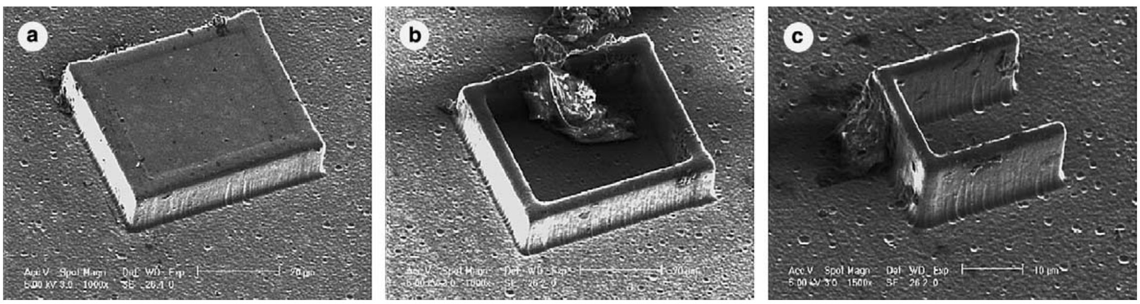

Fig. 3. SEM images of micromachined structures showing the effect of a (a) fully closed square outline, (b) small opening within the closed outline, (c) three out of four sides of the closed outline.

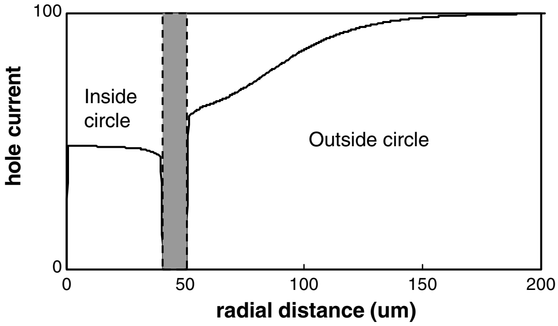

Fig. 4. MEDICI simulation showing the hole current, normalized to 100, as a function of lateral distance away from the centre of a 100 μm diameter closed circle, irradiated with 10 μm thick walls with 2 MeV protons. The irradiated region is shaded grey.

irradiated areas, where the resultant hole current and etching rate are reduced. In the low fluence irradiation, the edges of the dark, irradiated areas are blurred. This is interpreted as a significant hole current remaining at the edges of the irradiated areas, hence some lateral etching has occurred. The higher fluence irradiated lines are much darker and more uniform. This is because the hole current throughout the irradiated area is close to zero, resulting in abrupt interfaces. Hence the fluence dependence is important in fabricating well-defined patterned PSi, and also an important consideration for the Si micromachining work above.

3.2. Increased PL intensity from ion irradiated areas

We have also demonstrated that enhanced PL emission may be produced from irradiated areas of low resistivity p-type silicon. Studies by Gaburro et al. [32] showed that the PL intensity has a strong dependence on the resistivity of p-type silicon, with much higher PL intensity observed on samples with resistivity of 1–10 Ω cm compared to 0.01 Ω cm. We have used a 2 MeV proton beam to increase the local resistivity of a 0.02 cm p^+ silicon sample, thereby enhancing the light emission in the irradiated regions. By varying the proton fluence, the local resistivity is varied to obtain different PL intensities on a single silicon substrate. A variety of irradiated structures were fabricated with different fluences, and then electrochemically etched. Fig. 6 shows an optical and a PL image of various patterns irradiated with the same fluence, resulting in similar intensity PL emission.

The PL image in Fig. 7(a) shows structures patterned with the same geometry but irradiated with increasing fluences from right to left; the PL intensity obviously increases with fluence. Fig. 7(b) shows the measured PL intensity as a function of fluence. Initially, the PL intensity increases linearly with fluence, assumed to be due to the increased porosity of porous silicon formed on higher resistivity silicon [33]. Further increasing the fluence

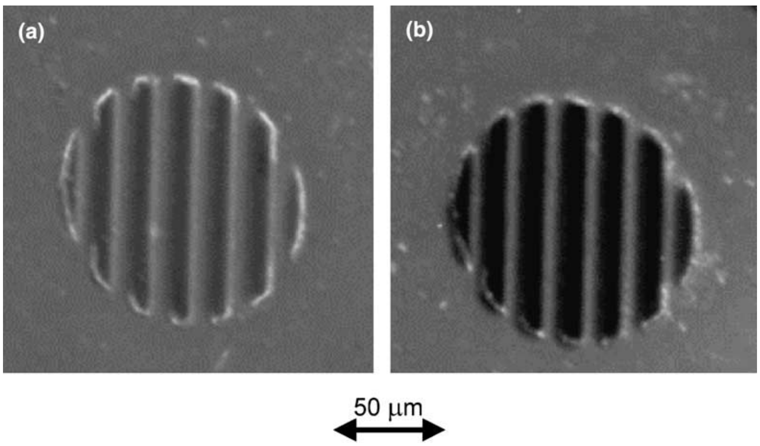

Fig. 5. Photoluminescence images of two areas patterned in a high-resistivity p-type silicon wafer with proton fluences of (a) 2.5×10^{14} and (b) $2.5 \times 10^{15}/cm^2$. Bright/dark areas correspond respectively to high/low recorded PL intensity.

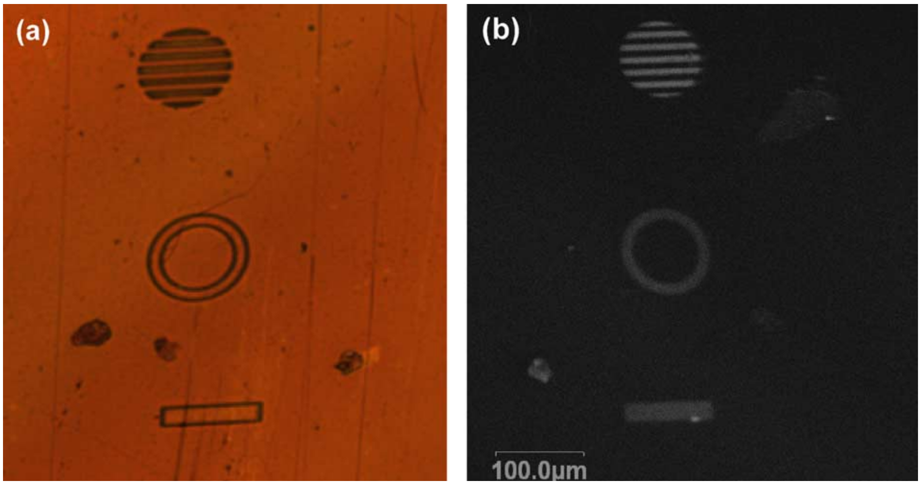

Fig. 6. (a) Optical, (b) photoluminescence image of various patterns irradiated with the same fluence. Bright/dark areas correspond respectively to high/low recorded PL intensity.

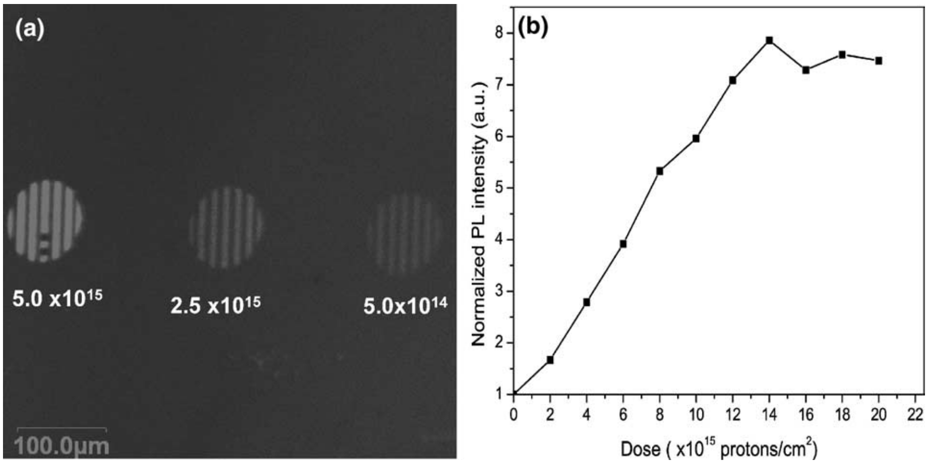

Fig. 7. Photoluminescence image of structures patterned with the same geometry but irradiated with increasing fluences from right to left. Bright/dark areas correspond respectively to high/low recorded PL intensity.

produces no change in PL intensity; this fluence decreases the carrier concentration by about 100 times at the end of range [25] corresponding to an increase in resistivity to $\sim 2\,\Omega$ cm. This result suggests that further irradiation with protons to increase the resistivity will not improve the light emission, in agreement with Gaburro et al. [32] who report that the PL intensity remains about the same for samples with 1 and $10\,\Omega$ cm resistivity.

4. Conclusions

Focused MeV ion beams in a nuclear microprobe may be used to produce high-aspect ratio, multilevel microstructures in silicon. The feature height of the irradiated structure can be accurately controlled with the fluence of the incident beam, enabling the production of a multilevel structure by multiple fluence exposures in a single irradiation step. It is important to consider the path of the electric field lines through the silicon wafer during electrochemical etching in order to correctly predict the form of the etched structure. MEDICI simulations are currently being used to do this.

We have also shown that patterned porous silicon may be fabricated in p-type Si using focused MeV ion beams in a nuclear microprobe. In high resistivity silicon, ion irradiation tends to produce patterned PSi with reduced PL intensity. In low resistivity silicon, focused proton beam irradiation can be used to selectively enhance the light emission in the irradiated regions. Tuning of the PL intensity has been obtained by controlling the local resistivity as a function of fluence.

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