Controlled intensity emission from patterned porous silicon using focused proton beam irradiation

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We have fabricated light emitting porous silicon micropatterns with controlled emission intensity. This has been achieved by direct write irradiation in heavily doped *p*-type silicon (0.02 Ω cm) using a 2 MeV proton beam, focused to a spot size of 200 nm. After electrochemical etching in hydrofluoric acid, enhanced photoluminescence is observed from the irradiated regions. The intensity of light emission is proportional to the dose of the proton beam, so the PL intensity of the micropattern can be tuned and varied between adjacent regions on a single substrate. This behavior is in contrast to previous ion beam patterning of *p*-type silicon, as light is preferentially created as opposed to quenched at the irradiated regions. © *2004 American Institute of Physics*.
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Porous silicon, formed by electrochemical etching of silicon in hydrofluoric (HF) acid, is of great interest due to its visible photoluminescence (PL) at room temperature and compatibility with standard microelectronics processes. The ability to emit light at energies greater than the silicon band gap of 1.1 eV is probably due to the quantum confinement effects produced by the low dimensionality of the silicon skeleton remaining after electrochemical etching.[1] There have been significant efforts to develop the material for fabrication of light emitting devices and its eventual integration into a microelectronic circuit.[2] Incorporation of patterned porous silicon directly onto a single silicon substrate with sufficiently high spatial resolution is required for such an application.

The most common method of patterning porous silicon is to use optical or electron beam lithography to define the pattern on the mask, so that only regions exposed to the HF solution will form porous silicon.[3,4] Another approach involves projecting a black and white image on the surface during etching, to selectively enhance or suppress pore formation.[5] Selective doping of the silicon is also shown to produce well-defined micropatterns of light emitting porous silicon.[6]

There have been several studies on ion beam irradiation for the production of patterned porous silicon. Schmuki and co-workers used a dose of $3\times10^{14}/\mathrm{cm}^2$ Si^{++} ions to irradiate *n*-type silicon, so that preferential pore formation was created at the defect sites when the sample was etched without illumination.[7–9] This technique allows one to write visible light emitting porous silicon down to submicron level. The opposite effect has been used to pattern *p*-type silicon whereby ion irradiation selectively quenches rather than produces light from the porous silicon.[10–12]

No prior patterning has shown preferential emission of light from irradiated regions of *p*-type silicon. In this work, we demonstrate that it is possible to do so by irradiating heavily doped *p*-type silicon. Earlier studies by Gaburro *et al.*[13] showed that the PL intensity has a strong dependence on the resistivity of *p*-type silicon. Much higher PL intensity was observed on samples with resistivity of 1–10 Ω cm compared to 0.01 Ω cm. Based on this relationship, we have used a highly focused, energetic proton beam to increase the local resistivity of a 0.02 Ω cm p^+ silicon sample, thereby enhancing the light emission in the irradiated regions. We show that direct writing of light emitting porous silicon microstructures can be achieved by focused proton beam irradiation and subsequent electrochemical etching.

Previously, we have used focused proton irradiation to selectively retard the rate of porous silicon formation so that free-standing microstructures are left behind after dipping in potassium hydroxide (KOH).[14,15] Here, the same technique is adopted except that the patterned porous silicon is not removed with KOH solution. The proton beam writing process was carried out at the Singletron Facility in National University of Singapore.[16] A 2 MeV proton beam, focused to 200 nm, was used to irradiate a heavily boron doped (0.02 Ω cm) silicon in a predefined manner.[17] These ions have a range of 48 μm in silicon, which is much greater than a penetration of few hundred nm for keV ions used in previous irradiation. This enables the production of a much thicker patterned porous silicon layer and therefore higher photoluminescence intensity. An electrical contact was made to the back surface using Ga–In eutectic and copper wire. Epoxy was used to protect the contact from the HF. The irradiated sample was then electrochemically etched in a solution of HF (48%): water: ethanol in the ratio of 1:1:2. After etching, the sample was briefly washed in distilled water and dried in air.

A sample was irradiated over an 80×80 $\mu\mathrm{m}^2$ area, with a fringe pattern at a dose of 2.5×10^{15} protons/cm^2 and subsequently etched at 37 mA/cm^2 for 5 min. UV confocal microscopy was performed using a 405 nm blue diode laser to image the patterned porous silicon. A 610 nm long-pass filter was placed in front of the photomultiplier tube so that the integrated PL intensity was collected from the porous silicon. The PL image of the fringe pattern in Fig. 1 shows clearly

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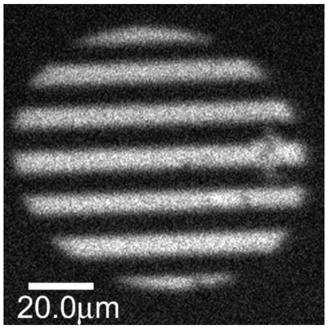

FIG. 1. PL image of a fringe pattern irradiated with 2.5×10^{15} protons/cm^2 and subsequently etched at 37 mA/cm^2 for 5 min.

that the bars irradiated with the proton beam appear brighter than the unirradiated regions.

In order to determine the emission properties of the irradiated and unirradiated regions, micro-PL spectroscopy was carried out on the fringe pattern using a 532 nm diode pumped solid state laser with an output power of 1–2 mW. The laser light was reflected off a red dichroic filter and focused onto the sample through a Leica DMLM microscope with a 100× objective. The PL signal was then detected using a CCD Ocean Optics Spectrometer via an optical fiber. Most of the laser light was cut off from the PL signal with the red dichroic filter and a 550 nm long-pass filter. Both spectra have been corrected for system response. Intense red luminescence with a peak wavelength of 750 nm has been observed from the regions irradiated with a dose of 2.5×10^{15} protons/cm^2 (Fig. 2). The spectrum has a broad full width half maximum of 200 nm, suggesting the presence of a wide distribution of pore sizes. The PL signal from the unirradiated regions is much lower. This is consistent with results by Gaburro *et al.*[13] where heavily doped *p*-type silicon exhibits very low PL intensity. As the ion beam penetrates the material, it creates lattice defects which act to trap the migrating holes, resulting in an increase in the local resistivity. It is shown in Fig. 2 that the resistivity change is significant enough to produce a peak intensity of 30× higher than the unirradiated regions.

By varying the dose of the proton beam, the local resistivity is varied to obtain different PL intensity on a single silicon substrate. The incident dose can be accurately controlled by the accumulated dwell time of the ion beam at each spot.[17] To demonstrate this, we have irradiated five vertical bars with 2, 4, 6, 8, and 10×10^{15} protons/cm^2 and

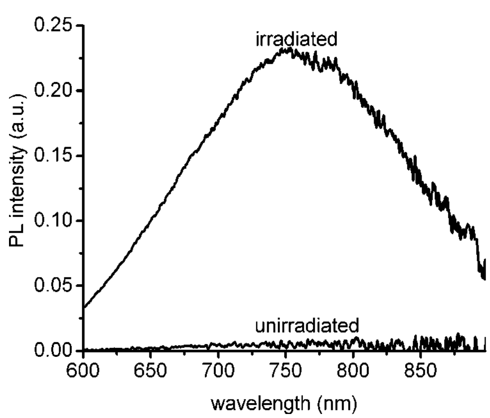

FIG. 2. Room temperature PL spectra of the irradiated and unirradiated regions in Fig. 1. Both spectra have been corrected for system response.

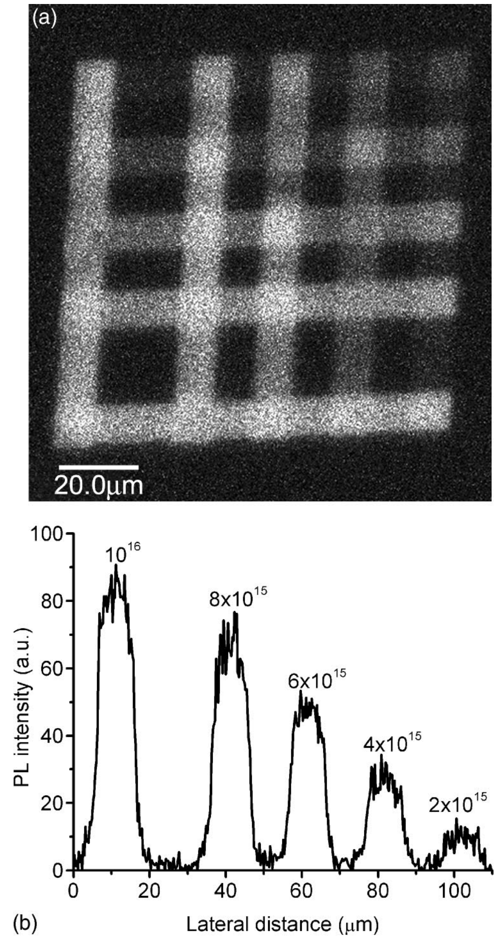

FIG. 3. (a) PL image of a checkerboard pattern irradiated with different accumulated doses; (b) line profile extracted across the five vertical bars with doses of 10, 8, 6, 4, and 2×10^{15} protons/cm^2.

overlapped them with similarly irradiated horizontal bars. The sample was then etched at 12 mA/cm^2 for 4 min. The bar irradiated with the highest dose was intentionally spaced at 20 μm instead of 10 μm for easy identification. This results in a checker board image whereby its intensity is representative of the dose at each region [Fig. 3(a)]. The horizontal and vertical bars, each measuring 10 $\mu\text{m} \times 100$ μm in dimensions, emit at higher intensity as the dose increases from top to bottom, and right to left. Regions where the bars overlapped also appear brighter in the form of squares. A horizontal line profile was extracted from the five vertical bars of the checker board image. The spatial variation of the PL intensity shows that there is a consistent increase in the intensity of the bar as the dose increases from 2×10^{15} to 10^{16} protons/cm^2 [Fig. 3(b)]. This demonstrates the ability to tune the PL intensity with the proton dose. It is found from the bar profile that a spatial resolution of 2 μm can be obtained with such a patterning technique.

In order to determine the PL dependency on dose, the intensity of each region is extracted from the checker board image and plotted in Fig. 4. Initially, the PL intensity is found to increase linearly by a factor of 8 as the dose increases from 2×10^{15} to 1.4×10^{16} protons/cm^2. This is assumed to be due to the increased porosity of porous silicon formed on higher resistivity silicon.[18] Further increasing the dose beyond 1.4×10^{16} protons/cm^2 produces no change in the PL intensity as saturation is reached. As significant amorphization of the crystal occurs at doses greater than

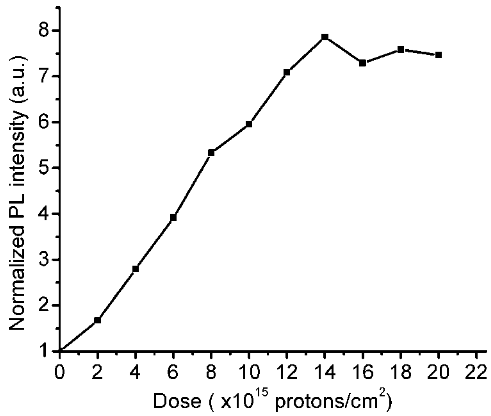

FIG. 4. Plot of the PL dependency vs dose for the irradiated pattern in Fig. 3.

10^{17} protons/cm^2, this does not account for the saturation. According to Yamaguchi *et al.*,[19] an irradiation of 1.4×10^{16} protons/cm^2 will decrease the carrier concentration by about 100$\times$ at the end of range, corresponding to an increase in resistivity to $\sim$2 Ω cm. This result suggests that further irradiation with protons to increase the resistivity will not improve the light emission since Gaburro *et al.*[13] reported that the PL intensity becomes independent of resistivity over the range 1–10 Ω cm.

In conclusion, focused proton beam irradiation prior to electrochemical etching of heavily doped *p*-type silicon has been used to selectively enhance the light emission in the irradiated regions. Tuning of the PL intensity has been obtained by controlling the local resistivity with doses up to 1.4×10^{16} protons/cm^2.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] K. D. Hirschman, L. Tsybeskov, S. P. Duttagupta, and P. M. Fauchet, Nature (London) **384**, 338 (1996).
[3] A. G. Nassiopoulos, S. Grigoropoulos, L. Canham, A. Halimaoui, I. Berbezier, E. Gogolides, and D. Papadimitriou, Thin Solid Films **255**, 329 (1995).
[4] S. P. Duttagupta, C. Peng, P. M. Fauchet, S. K. Kurinec, and T. N. Blanton, J. Vac. Sci. Technol. B **13**, 1230 (1995).
[5] V. V. Doan and M. J. Sailor, Appl. Phys. Lett. **60**, 619 (1992).
[6] A. J. Steckl, J. Xu, H. C. Mogul, and S. Mogren, Appl. Phys. Lett. **62**, 1982 (1993).
[7] P. Schmuki, L. E. Erickson, and D. J. Lockwood, Phys. Rev. Lett. **80**, 4060 (1998).
[8] P. Schmuki and L. E. Erickson, Appl. Phys. Lett. **73**, 2600 (1998).
[9] L. E. Erickson and P. Schmuki, and D. J. Lockwood, J. Vac. Sci. Technol. B **16**, 3301 (1998).
[10] J. C. Barbour, D. Dimos, T. R. Guilinger, M. J. Kelly, and S. S. Tsao, Appl. Phys. Lett. **59**, 2088 (1991).
[11] X. M. Bao and H. Q. Yang, Appl. Phys. Lett. **63**, 2246 (1993).
[12] T. M. Bhave, S. V. Bhoraskar, S. Kulkarni, and V. N. Bhoraskar, J. Phys. D **29**, 462 (1996).
[13] Z. Gaburro, H. You, and D. Babic, J. Appl. Phys. **84**, 6345 (1998).
[14] E. J. Teo, M. B. H. Breese, E. P. Tavernier, A. A. Bettiol, F. Watt, M. H. Liu, and D. J. Blackwood, Appl. Phys. Lett. **84**, 3202 (2004).
[15] E. J. Teo, E. P. Tavernier, M. B. H. Breese, A. A. Bettiol, F. Watt, M. H. Liu, and D. J. Blackwood, Nucl. Instrum. Methods Phys. Res. B **222**, 513 (2004).
[16] F. Watt, J. A. van Kan, A. A. Bettiol, T. F. Choo, M. B. H. Breese, and T. Osipowicz, Nucl. Instrum. Methods Phys. Res. B **210**, 14 (2003).
[17] A. A. Bettiol, J. A. van Kan, T. C. Sum, and F. Watt, Nucl. Instrum. Methods Phys. Res. B **181**, 49 (2001).
[18] S. Hilbrich, W. Theiss, R. Arens-Fischer, O. Gluck, and M. G. Berger, Thin Solid Films **276**, 231 (1996).
[19] M. Yamaguchi, S. J. Taylor, M. J. Yang, S. Matsuda, O. Kawasaki, and T. Hisamatsu, J. Appl. Phys. **80**, 4916 (1996).