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# New developments in the applications of proton beam writing

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#### Abstract

This report describes how proton beam writing can be used to produce direct write, high resolution three dimensional structures on the nano and micron scales in semiconductor materials such as p-type (100) bulk silicon and gallium arsenide. The lattice damage caused by the proton irradiation increases the electrical resistance of the semiconductors resulting in a raised structure of the scanned area after an electrochemical etch.

Advances in this field over the past few years and its relevance to future technology mean that it is now a powerful contender for direct write technology for future nodes 45 nm and below. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

The 2003 International Technology Roadmap for Semiconductors (ITRS) now recognises direct write and imprint technology as potential lithographic techniques for technology nodes of 45 nm and below and states that although these technologies are still very much in the research stage "breakthroughs in direct-write technologies that achieve high throughput will be a significant paradigm shift. It will eliminate the need for masks, offering inherent cost and cycle-time reduction" [1].

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One of the new generation of direct write techniques is proton beam writing (PBW). Proton beam writing offers significant advantages compared to other techniques, such as electron, X-ray, and focused ion beam lithography. Electrons suffer from significant scattering on their way through matter due to their low mass. This produces a poor aspect ratio in the structures created by electron beam writing (e-beam writing), even though these beams can produce structure of very small lateral dimensions. In thick films, the minimum feature size is comparable to the film thickness, making electron-beam lithography essentially a two dimensional process. LIGA (Lithographie, galvanoformung und abformung, the German words for Lithography, Electroplating and Molding) uses highly collimated beams of X-rays (usually from a synchrotron or storage ring). This has the advantage of producing deep high aspect ratio structures, but requires the use of a mask and access to a synchrotron light source which is both expensive and time consuming. Focussed ion beams (FIB) use low energy heavy ions (e.g. 30 keV Ar) to erode the structure atom by atom (sputtering), and although this technique can be used to produce three dimensional structures it is relatively slow and there may be problems with the re-deposition of the sputtered atoms.

A major advantage of proton-beam writing compared to these other techniques is the long well-defined range of the high-energy protons in matter, in the order of tens of microns (depending on the proton energy and the target material). This makes it possible to create deep high-aspect ratio structures. As there is no need for a mask, this technique is ideal for the rapid prototyping of three-dimensional structures.

The speed and compatibility of proton beams with ultra large scale integration (ULSI) fabrication makes proton-beam writing a very promising candidate for development in this field. Moreover, proton-beam writing offers an attractive solution for the fabrication of X-ray masks which will be required if X-ray lithography is going to be used for future generations of devices.

This paper reports on the use of p-beam writing on semiconductor substrates (GaAs and Si) to create structures of both micro and nano dimensions.

# 2. Experimental

Proton-beam writing in (100) p-type gallium arsenide (GaAs) with sheet resistance  $1.1 \times 10^{-2}$ –  $1.3 \times 10^{-2} \Omega/sq$  was carried out using the microbeam line [2] at the University of Surrey Ion Beam Centre. At Surrey a 3 MV High Voltage tandetron accelerator is used to accelerate the high energy ion and proton beams. The beam focusing system comprises of an Oxford triplet system of magnetic quadrupole lenses which can produce a beam diameter of  $1-2 \mu m$  in vacuum.

Proton-beam writing in (100) p-type silicon with nominal resistivity of  $15 \,\Omega \,\text{cm}$  was carried out in the Centre for Ion Beam Applications (CIBA) at the National University of Singapore (NUS) [3]. The CIBA group used a high brightness, 3.5 MV single-ended accelerator [4] from high voltage, and have attained a minimum beam resolution of 35 nm [5] using a high demagnification focusing triplet and the magnetic scanning system of Oxford Microbeam Ltd. [6]. The CIBA group have developed a scanning software [7] which has a resolution of up to 4000 pixels which is currently being installed at Surrey. The structures produced at Surrey were made using a lower scanning resolution of 256 pixels.

Previous proton beam writing has been performed on different polymers such as PMMA [8– 10]. Semiconductor materials have a higher electrical resistance compared to them so they require larger doses resulting in a longer irradiation periods. Nevertheless the time required for irradiation is relatively short, ranging from a few to 30 min.

## 3. Etching

Etching is the procedure used to reveal the irradiated structures. Semiconductor materials present a "negative" behaviour towards etching. This means that the irradiated regions remain intact because the lattice damaged region prevents the transport of holes which is the basis of the electrochemical etch [11]. Different chemical electrolyte mixtures are used for different semiconductor materials.

# 3.1. Etching gallium arsenide (GaAs)

For GaAs the irradiated sample is electrochemically etched in an electrolyte mixture of one part of Tiron (4,5-dihydroxy-*m*-benzenedisulfonic acid, di-sodium salt) and 30 parts of deionised water. An electrical current of  $10 \text{ mA/cm}^2$  is passed through the sample which generates OH<sup>-</sup> ions on the platinum cathode while the GaAs acts as the anode. The reaction that occurs on the GaAs surface causes the GaAs to be oxidised and etched. The irradiated regions are damaged by the incident proton beam and thus inhibit hole transport during electrochemical etching. Consequently the non-irradiated regions are preferentially etched [11].

Fig. 1 shows the basic steps of electrochemical etching of GaAs.

- (a) Patterning of p-type GaAs with proton beam writing. Proton irradiation causes lattice damage, producing deep regions of high electrical resistivity. This causes a reduction in hole flow within the material.
- (b) This electrochemical etch is driven by the flow of current through the GaAs material. A Tiron electrolyte solution is used in this etch in order to get a constant current flow leading to the dissolution of the implanted material.
- (c) Once the sample has been taken out of the electrochemical etch setup and immersed in deionised water the region where the protons have irradiated is then revealed.

### 3.2. Etching silicon (Si)

For silicon the irradiated sample is electrochemically etched in an electrolyte mixture of hydrofluoric acid:water:ethanol (1:1:2). An electrical current of 40 mA/cm<sup>2</sup> is passed through the wafer which causes the formation of 'porous silicon' at the surface [12,13]. The regions of defects, caused by the proton irradiation, inhibit the formation of porous Si. After electrochemical etching, the porous Si is removed using a diluted potassium hydroxide (KOH) solution, leaving the final patterned structure on the wafer surface as a 3D representation of the scanned pattern area and fluence. This is shown in Fig. 2 [14,15].

- (a) Patterning of p-type silicon with proton beam writing.
- (b) Electrochemical etching to selectively form porous silicon in un-irradiated regions.



Fig. 2. The Basic steps of electrochemical etching of Si.



Fig. 1. The Basic steps of electrochemical etching of GaAs.

(c) Removal of porous silicon with diluted KOH solution.

# 4. Results and discussion

Fig. 3(a) and (b) below are scanning electron micrograph (SEM) images of a series of parallel wall structures of decreasing lengths produced in p-type GaAs at the University of Surrey. These structures were created using a proton beam with an energy of 2.5 MeV and a fluence of  $8 \times 10^{15}$  protons/cm<sup>2</sup>. The sample was then etched for 2 h with a current density of 10 mA. This produced wall heights of approximately 13 µm. Using this energy of 2.5 MeV, SRIM simulations [16] indicate that the protons penetrate  $\sim 45 \,\mu m$  into the GaAs. The reason why the structure has not been etched to reveal the full range of the protons is due to the slow etch rate ( $\sim 0.1 \,\mu$ m/min using a current of 10 mA). Fig. 3(b) is a close up of the boxed region in Fig. 3(a). The rounding of the edges may be due to the etching procedure and is currently under investigation.

Fig. 4(a) and (b) are the structures produced by CIBA at the National University of Singapore using proton and helium beams in Si. A fuller account of this work may be found in [3,14,15]. Fig. 4(a) shows a scanning electron micrograph (SEM) of a uniform array of closely packed, high aspect ratio pillars obtained by single spot irradiations of a focused proton beam. Each spot has an accumulated fluence of  $5 \times 10^{16}$  protons/cm<sup>2</sup>. The

sample was then etched for 15 min with a current density of 40 mA/cm<sup>2</sup>. The pillars are 4.5  $\mu$ m high



Fig. 4. (a) Array of high aspect-ratio pillars obtained by single spot irradiations. Inset picture shows the profile of the pillars. Structures produced using a proton beam. (b) Multi-level cross structures irradiated with multiple doses of He ions.



Fig. 3. (a) SEM image of variable length wall structure made in GaAs. (b) SEM close-up image of the variable length wall structure in GaAs.

with a diameter of  $0.6 \,\mu\text{m}$ , and a periodicity of 2  $\mu\text{m}$ . The profile of the pillar reveals vertical and smooth sidewalls with slight broadening at the base [3,15].

Fig. 4(b) shows a multi-level cross structure generated by irradiating by  $6 \times 10^{14}$ ,  $2.5 \times 10^{15}$  and  $1.9 \times 10^{16}$  He/cm<sup>2</sup> doses of 2 MeV helium ions. The raised portions of the structure were produced using higher beam doses than the surrounding large cross. Undercutting of the structure can be seen around the outer edge of the cross as the sample is etched beyond the end of range, enabling the formation of cantilever structures [3,14].

# 5. Conclusion

High resolution three dimensional structures on the nano and micron scales have been successfully produced in the semiconductor materials such as silicon and gallium arsenide using the proton beam writing. Advances in this field over the past few years and its relevance to future technology means that it is now a powerful contender for direct write technology for future nodes of 45 nm and below. Its versatility and speed also make it useful for proof of concept "one of" devices.

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