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# Materials Patterning and Characterisation at the Nanometre Scale Using Focused MeV Ion Beams: Present Achievements and Future Prospects

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A key phenomenon in the interaction of MeV ions and solids is that the energy transferred from the primary ions to the target electrons is high compared with atomic and molecular binding energies, but low compared with the ion energy. This means that there is a high probability of modifying the chemical properties of the material (for patterning) or of inducing the emission of electromagnetic radiation (for analysis), yet the path of particle is changed by a negligible amount, which means that focused beams remain sharp even after penetrating long depths into the material. Developments in focusing MeV ions in recent years have pushed the useable beam diameters into the sub-micrometre region, which means that nuclear microbeams are poised to make an impact in both direct write fabrication and micro-analysis at length scales of interest in nanotechnology or microbiology. This paper reviews the science and technology underlying the use of nuclear microbeams (ion solid interactions, focusing systems) and reports on the present status and trends of applications in sub-micron scale applications.

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## 1. Interactions between MeV ions and atoms: the key advantage of MeV ions in nanoscale applications

MeV ions interact with the atoms of target materials through electrostatic forces between the charged electrons and nuclei of the atoms. Apart from a small fraction of ions which undergo large angle scattering resulting from a close approach to the nucleus (the Rutherford scattering), the primary effect of the interaction is to create a transient electric dipole excitation of the electron structure of the atom. Kinetic energy is absorbed from the ion and may result in ionisation or promoting one or more of the atomic electrons into excited states.

The energy transferred from the ion to the atom depends on many factors, but can range from zero to a few tens of keV. This is *large* compared with electronic binding energies (especially those of valence electrons), giving a high probability of locally modifying the chemistry of the sample, but *small* compared with the primary ion energy, so that the ion is not strongly deflected or decelerated, and can undergo many thousands of atomic collisions while following an essentially straight path for a large part of its range.

This is the unique advantage of MeV ions for high spatial resolution applications: there is a high probability of creating useful effects in the material, yet the primary ion has a long range and a straight path with low lateral scattering. This is demonstrated in Fig. 1, which shows a SRIM 2008 [1] simulation of the paths of 1000 3 MeV protons in poly(methyl methacrylate) (PMMA) photoresist; the beam diameter remains less than 1 $\mu$m at up to 50 $\mu$m within the sample.

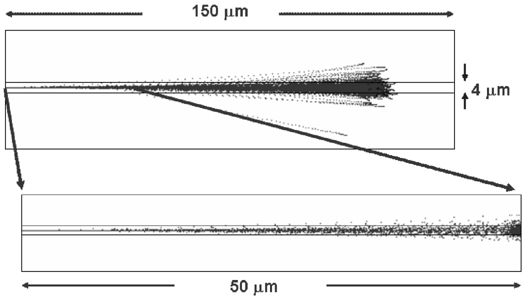

Fig. 1. SRIM 2003 simulations of the paths of 1000 3 MeV protons incident on a PMMA surface. The inset shows an expansion of the region down to 50 $\mu$m, demonstrating that the majority of the beam is contained within a 1 $\mu$m diameter cylinder.

The effects induced by the beam include the following:

- Chemical modification of the sample due to molecular bond-breaking. This is particularly significant in organic materials and polymers and can lead to effects as diverse as increased solubility due to chain scission, reduced solubility due to polymer cross-linking and damage to biological molecules such as DNA.
- Modification of refractive index in transparent materials.
- Emission of characteristic electromagnetic radiation, which can be used for characterisation of the material. X-rays resulting from inner shell ionisa-

tion lead to the well-known technique of particle induced X-ray emission (PIXE).

- Creation of electron–hole pairs allowing charge induction in semiconductor junctions.

In addition, the nucleus may also acquire kinetic energy, resulting in atomic displacements or lattice heating. This can lead to:

- Modification of magnetic properties.
- Modification of carrier mobility in semiconductors.
- Sample heating.

The minimum spatial extent of the effects caused by a single ion is defined by the *ion track*. This is a cylinder of short-lived high temperature plasma surrounding the entire length of the ion path (see Fig. 2). Energetic secondary electrons (delta rays) created by ionisation travel laterally from the beam and induce further effects on the material. The diameter of the ion track, which is defined by the range of the delta rays depends on the energy and species of the primary ion [2, 3], but is typically less than 10 nm. All the primary effects of the ion on the material are confined within this diameter which represents the limiting spatial resolution of MeV ion beam techniques. Let us note that this is in the nanometre range, which indicates that MeV ions have an exciting potential for nanotechnology applications.

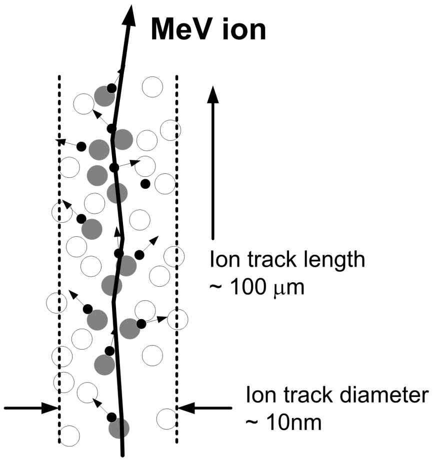

Fig. 2. Schematic diagram showing the formation of a ion track by the passage of an energetic ion through matter. Grey circles represent ionised atoms and black dots indicate the energetic secondary electrons (delta rays) responsible for further ionisation.

## 2. Modes of using MeV ions

MeV ions can be exploited in two modes of operation (see Table). In single ion methods (precisely positioned single ions, PPSI), counted numbers of single ions are directed to a selected point in the sample. In this way, the full potential of single ion track diameters can be realised. In continuous beam (CB) methods, a beam of many ions per second is focused to a small diameter and directed onto the sample. This mode allows interactions with lower probability to be exploited (e.g. X-ray emission, photoresist exposure).

TABLE

A comparison of the two modes of utilising high energy ions for materials modification or characterisation.

| Mode | Description | Equipment issues |
|---|---|---|
| precisely positioned single ions (PPSI) | direct individually counted ions to preselected points on the sample to exploit single ion track effects | • targeting accuracy of single ions (focusing, positioning);<br>• counting accuracy |
| continuous beam (CB) | confine a beam of many particles/s within a small region of the sample to exploit low probability effects | • beam spot diameter;<br>• achievable current |

Both these modes of operation require the use of a device to focus or target the beam, ideally to dimensions comparable with the ion track diameter. In the PPSI mode, the important parameters are the targeting accuracy and the accuracy of ion counting. In CB mode, the critical parameters are the focused beam diameter and the available beam current, which will determine the time required to carry out a particular experiment.

## 3. Focusing MeV ions to sub-micron dimensions

The high momentum of MeV ions which gives them their advantage for high resolution applications also makes them difficult to focus. In particular, the standard cylindrical magnetic and electrostatic lenses used in electron or low energy ion focusing columns are too weak to be used with MeV ions, and alternative technologies must be sought. Many different arrangements of apertures and electromagnetic fields have been proposed, but the system which has shown consistently the best performance is the magnetic quadrupole multiplet [4].

Quadrupole lenses have four magnetic poles arranged symmetrically N–S–N–S around the beam axis. They have a strong focusing action on charged particle beams, but because of the antisymmetry, a single quadrupole lens converges the beam only in one plane and diverges in a plane normal to this. For this reason two or more quadrupoles of alternating polarity are required to form a point focus. Combinations of two, three and four lenses have been used (see Fig. 3).

MeV ion microbeams based on magnetic quadrupole lenses are installed in many institutions, though at present, the usable beam diameter (targeting accuracy) routinely available is of the order of a few micrometres,

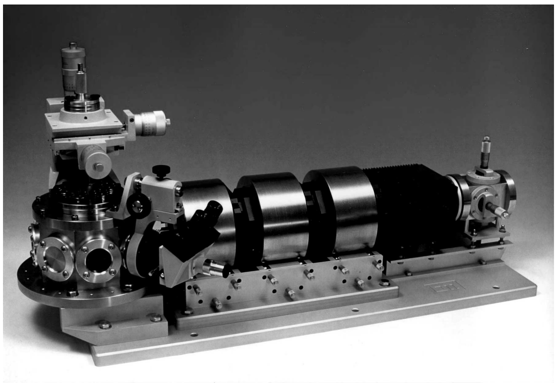

Fig. 3. Photograph of the end stage of a commercially available microbeam focusing system using a triplet of magnetic quadrupoles. The beam enters the system from the right and passes through the collimator aperture, magnetic deflection coils to sweep the beam across the sample and the three quadrupole magnets before entering the target chamber where the sample is mounted on a micrometer controlled positioning stage (Oxford Microbeams Ltd., Oxford, U.K.).

still orders of magnitude greater than the limiting ion track diameters. This is perhaps surprising, given that the first 1 $\mu$m beam was reported in 1981 [5]. The reasons for this apparent non-compliance with Moore's law are predominantly practical. Ions in the low MeV energy range are usually generated using a small electrostatic accelerator such as a Van de Graaff or tandetron type. Other types of accelerator such as cyclotrons or heavy ion linacs are generally uneconomical at the relatively low energies required for routine ion beam applications and may also have beam properties, particularly energy spread, which are detrimental to micro-focusing. The environment of a nuclear accelerator facility is inherently noisy (both mechanically and electromagnetically), while at the same time, a high standard of precision and stability is required in the construction and alignment of the components. Thus it is a major engineering challenge to construct a high precision nanoscale instrument in such a location.

In addition to this, there are more fundamental constraints associated with (1) the properties of the beams available from nuclear accelerators (brightness, energy stability), which means that focusing systems must have a relatively large angular acceptance in order to transmit a useful current and (2), most importantly, the problems of fabricating small (few micrometre diameter) apertures in material thick enough to stop MeV ions. These apertures are used to define the "object" of the probe-forming system, and in nanobeam systems, these may have to have diameters of less than 10 $\mu$m. Penetration of the ions through the edges of the aperture allows ions with reduced energy and random direction to enter the focusing system, leading to a "halo" of beam surrounding the final spot. The magnitude of this slit scattering effect increases as the aperture is reduced (to obtain smaller spot diameters) and sets a limit to the ultimate spatial resolution.

Already though, a small number of facilities have demonstrated that useable beam diameters of less than 100 nm can be achieved (e.g. [6, 7]) and several groups are working on the design of the next generation of quadrupole focusing systems (e.g. [8–10]), often involving high demagnification multiple stage lenses. There is the exciting possibility that sub-100 nm beams will be routinely available in the near future.

## 4. Applications of PPSI

Single ions for PPSI applications can be generated using a very fast beam switch (electrostatic deflector) upstream of the focusing system. If the beam flux is reduced to a small number of particles per second (typically 1000 $s^{-1}$) then the beam switch can be used to block the beam when a signal is received to indicate that a ion has struck the target, thus preventing any more ions reaching the target [11]. The major technical challenge for this technology is in generating the "ion hit" signal. For samples transparent to ions, this can conveniently be obtained from a semiconductor detector behind the sample, but for thick samples a variety of methods are being developed which rely on the detection of secondary electrons, optical luminescence or charge induced by the ion.

The potential applications of PPSI can be considered under the following three headings.

### *4.1. Ion track lithography*

This technique exploits the change in solubility created in the track of single ions in polymer materials. By etching the exposed material, a "nanotube" with diameter of a few nanometres and length determined by the length of the path of the ion can be created. This can either be exploited directly, for example as a filter membrane, or can be used as an electroplating template to form a nanowire. At present spectacular results are being obtained at GSI, Darmstadt, using high LET (GeV) heavy ions, with energies outside the scope of this review (e.g. [12]). However, this is likely to be a fruitful area of research using precisely positioned ions with the lower energies available from small tandem accelerators (e.g. 10–20 MeV $^{12}$C ions) and could offer the exciting potential of forming regular arrays of such wires, which may have, for instance, novel optical or magnetic properties.

### *4.2. Quantum implantation*

The fundamental unit of a quantum computer, or qubit can be created by implanting two electrically active impurity atoms into a semiconductor spaced so closely that their wave functions overlap. Such devices are already being constructed using masked implantation of low energy ($\approx$ 30 keV) phosphorus atoms into silicon [13]. Although the ion energy required for this application is less than that normally encountered in MeV ion beam systems, PPSI may have an important potential in fabricating optical or electrical quantum arrays or quantum dots by implanting groups of active impurity ions in closely spaced regular arrays.

### *4.3. Cell probes*

An increasingly important application of PPSI is the use of counted single ions to explore the response of living cells to damage by radiation. Single ions are directed to selected regions (e.g., nucleus, cytoplasm) of selected living cells in a culture. The subsequent response of the cell or the entire colony can be used to obtain information which could be applied to the optimisation of radiotherapy treatments for cancer or the understanding of the health risks of low dose radiation exposure [14]. This technique has been used for several years using fixed collimated beams and a moving target stage, but the development of PPSI with rapidly steered focused beams offers the potential of a much faster irradiation rate, which will be important in exploring low probability effects. New facilities using PPSI are operational or under construction (e.g. [15, 16]), including the vertical tower system at the University of Surrey, in which the ion focusing system, sample stage and optical microscopy are mounted at the top of a 10 m high tower into which the beam from the horizontal accelerator is injected through a 90° bending magnet [17, 18].

Cell probe applications of MeV ions are described further by Pallon in these proceedings [19].

## 5. Applications of continuous beams

In principle, any application of focused ions already available with conventional MeV continous beam ion microbeams can be extrapolated to the nanometre scale using a nanobeam focusing system. In particular, ion beam microanalysis (PIXE, RBS [20]), which is probably the major application at present, could be expected to yield results, for example, on the sub-cellular scale (e.g. [21, 22]). It is likely that the beam current in nanobeam systems will be less than that in the microbeams, so unless larger solid angle detectors can be used, the signal rate will be lower. In addition, the higher current density of the nanobeam may create problems with sample damage, so at this stage it is too early to assess the importance of ion beam analysis with nanobeams.

However, one application which will become increasingly important at small beam diameters is MeV ion lithography. As noted above, MeV ions follow virtually straight paths for the majority of their range in matter. This fact is the basis for the newly emerging field of MeV ion lithography or proton beam writing (PBW). Studies have found that the majority of materials which are sensitive to other forms of radiation (e.g. photoresist, electron beam resists) respond in a similar way to MeV ion irradiation, although in some cases the total deposited energy required to expose the material may be different (in most cases, less). The technique was first demonstrated in PMMA [23], but is being extended to other materials including negative working SU-8 resist, UV sensitive etchable glasses and semiconductors.

PBW can create structures with depths of tens of micrometres with a side-wall angle very close to 90 degrees and very low roughness (1–10 nm) and is at present *the only single-step direct write lithography* capable of fabricating three-dimensional structures with sub-micron feature sizes and could become a significant tool in the development of semiconductor and other devices in the sub-100 nm range.

Figure 4 shows the processes involved in proton beam writing using positive and negative resist materials. Negative resists (Fig. 4b) give the unique possibility of exposing the material at different energies to create overhanging structures or buried channels. One of the major centres for the development of PBW is the National University of Singapore [24], though an increasing number of other facilities are working in this area.

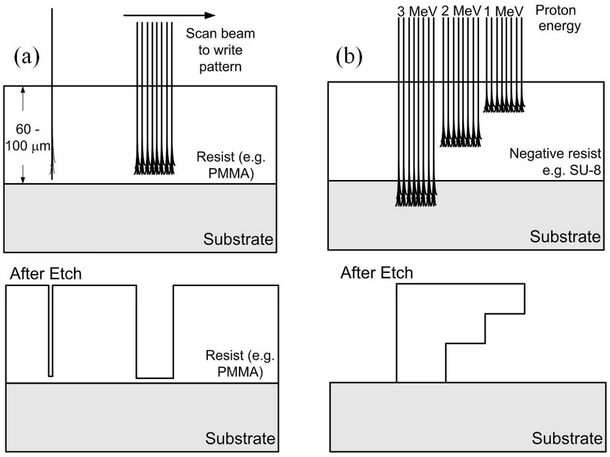

Fig. 4. Schematic diagram showing the principles of proton beam writing in (a) positive resist material (material becomes soluble in the beam) and (b) negative resist material, showing how a negative material can be exposed at different energies to fabricate cantilevered structures with controlled thickness.

At the time of writing the full potential of PBW is still being explored, and the quality of the demonstration structures which can be formed are indicated in Fig. 5.

Specific areas of application for PBW will include microfluidics, where the three-dimensional capability of the technique can be exploited to fabricate buried micro--channels in a single exposure step [25] (see Fig. 6), for complex surface texturing for tissue engineering and surface biotechnology applications [26] and the fabrication of micro-optical structures such as waveguides, couplers, photonic bandgap filters, etc.

A key industrial role for PBW is expected to be in the fabrication of stamp masters for nano-imprint lithography, which can then be used to replicate many devices,

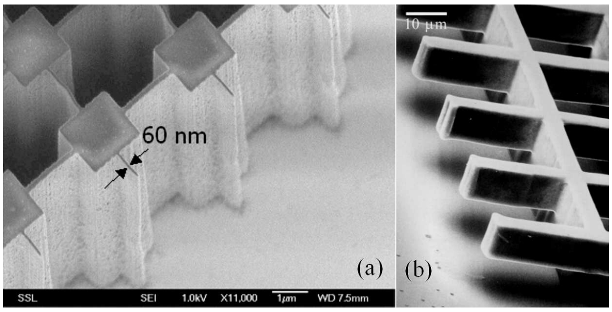

Fig. 5. Demonstration structures formed in SU-8 negative photoresist using proton beam writing with beams of MeV protons. (a) Pillars 1 $\mu$m in diameter and 10 $\mu$m high joined by walls with a thickness of 60 nm formed using a beam of 1 MeV protons focused to a diameter of 60 nm. (b) Cantilevered structure formed by exposing SU-8 with protons of 2 MeV to form the walls and 1 MeV protons to form the cantilevers (courtesy of CIBA, National University of Singapore).

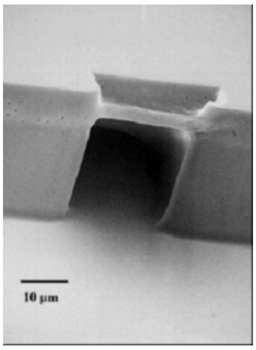

Fig. 6. A buried channel for use in a microfluidic network formed in a SU-8 negative photoresist by dual energy proton beam exposure: 2.5 MeV to form the walls and 1 MeV for the channel cap (courtesy of CIBA, National University of Singapore).

including masks for X-ray (LIGA) and extreme ultraviolet (EUV) lithography [27]. This combination of technologies will combine the high aspect ratio, small feature size and short development cycle of PBW with the volume production capabilities of conventional techniques.

## 6. Conclusion

This article aims to demonstrate that the unique properties of the interaction between MeV ions and atoms gives the possibility of materials modification or characterisation with a lateral scale in the nanometre region, the lower limit being determined essentially by the diameter of the ion tracks in the material. Focusing systems capable of targeting continuous beams or single ions to this sort of resolution are currently under development and an exciting range of novel applications of both continuous beams and precisely positioned single ions is emerging.

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