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Three-dimensional nanolithography using proton beam writing

J. A. van Kan,[a)] A. A. Bettiol, and F. Watt
Centre for Ion Beam Applications (CIBA), Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

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We report the utilization of a focused mega-electron-volt (MeV) proton beam to write accurate high-aspect-ratio structures at sub-100 nm dimensions. Typically, a MeV proton beam is focused to a sub-100 nm spot size and scanned over a suitable resist material. When the proton beam interacts with matter it follows an almost straight path. The secondary electrons induced by the primary proton beam have low energy and therefore limited range, resulting in minimal proximity effects. These features enable smooth three-dimensional structures to be direct written into resist materials. Initial tests have shown this technique capable of writing high aspect ratio walls of 30 nm width with sub-3 nm edge smoothness.
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In many fields there is a growing interest in high-resolution, high-aspect-ratio lithography, e.g., microphotonics, micro/nanofluidics, and nanoimprinting. Although electron beam (e-beam) writing is utilized effectively in many sub-100 nm applications, it is intrinsically difficult to produce submicron structures of high-aspect ratio because electrons scatter as they penetrate the resist. In this letter we present a sub-100 nm lithography technique which utilizes mega-electron-volt (MeV) protons. In this technique, which we have named *p-beam writing*, the path of a MeV proton in material is dependent on the interaction with the electrons and nuclei in the material. The probability that a proton interacts with an electron is a few orders of magnitude larger than for nuclear scattering in the first 50% of its trajectory. Because of the high mismatch in mass between the proton and the electron ($m_p/m_e \sim 1800$), proton-electron interactions do not result in any significant deviation in the trajectory of a proton from a straight line path. Further, due to the momentum mismatch, the energy transfer in each proton/electron collision is small. Consequently, since many thousands of collisions will occur before a proton comes to rest, proton trajectories and energy loss profiles can be accurately simulated by means of Monte Carlo calculations (for example using the computer code SRIM).[1] It should be noted that p-beam writing is different from focused ion beam (FIB) technology, in that FIB is a relatively slow machining process which utilizes the impact of low energy (kilo-electron-volt) heavy ions to sputter ions from the surface of a material.

We have used two common resist materials in our investigations so far. In the exposure of poly(methylmethacrylate) (PMMA), the protons cause chain scissioning of the polymer chains. The resulting damaged resist, consisting of molecular chains with lower molecular weight, are then selectively removed using a suitable chemical developer at 30 °C.[2] PMMA therefore is a positive resist under proton irradiation. On the other hand SU-8, (a chemically amplified, epoxy based resist) crosslinks under proton beam exposure. A suitable chemical developer can then be employed at room temperature to selectively remove the unexposed areas,[3] making SU-8 a negative resist under proton beam exposure. The most suitable fluence to expose PMMA with 2 MeV protons is 80 nC/mm^2. In the case of SU-8 only 30 nC/mm^2 is needed for full crosslinking.

We have identified several key features that make p-beam writing a lithographic technique of high potential: (a) Protons have a relatively long and well defined range in resist materials. The penetration depth depends on the proton energy; e.g., the penetration of a proton beam of energy 1.0 MeV in PMMA is 20 μm, whereas a 3.5 MeV proton will penetrate 160 μm.[1] This feature allows the production of slots and holes of well defined depth, and the creation of multilevel structures in one resist layer.[4,5] By exposing the negative resist SU-8 to protons at different energies, structures can be produced in one layer of resist. These structures include buried microchannels, cantilevers, etc.[4,6] (b) The proton beam travels in a straight line, with very little small angle scattering except at the end of range. This allows the production of structurally accurate high aspect ratio structures. SRIM calculations[1] show that a point like 0.5 MeV proton beam penetrating a 200-nm-thick PMMA layer applied on a silicon substrate will spread and have a radius of less than 1.0 nm when it enters the silicon substrate. The generated secondary electrons (delta rays) will have a typical range of 1.4 nm, in which 90% of the electron energy is deposited.[7] This confinement coupled with an even energy deposition along the path of the proton beam generates smooth sidewalls. Our calculations show that lithography with MeV protons is potentially capable of producing high quality nano- and microstructures with 1 nm smoothness and high aspect ratio. (c) The proton beam has a relatively even dose distribution with penetration depth. Monte-Carlo calculations using SRIM[1] show that the energy deposition increases slowly with depth, and increases rapidly only at the end of range where energy loss due to proton/nuclear collisions increase. This feature ensures a relatively even exposure distribution with depth.

[a)]Electronic mail: phyjavk@nus.edu.sg

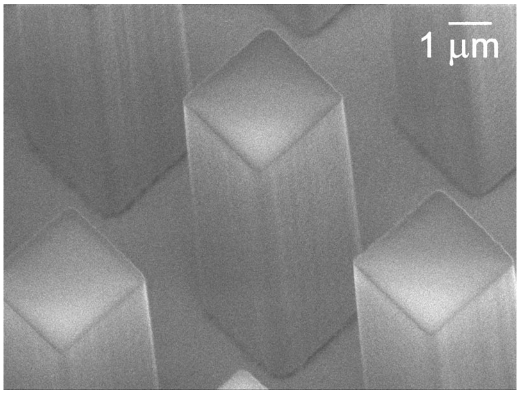

FIG. 1. SEM image of $3\times3\ \mu m^2$ pillars in a 10-μm-thick SU-8 layer. These structures were written with a focused 2 MeV proton beam.

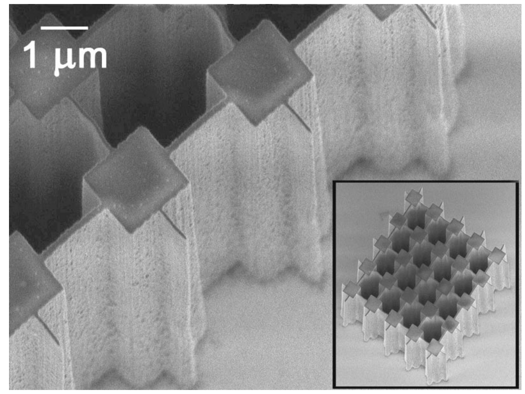

FIG. 2. SEM image of $2\times2\ \mu m^2$ pillars written in a 10-μm-thick SU-8 layer (inset). Linking the pillars are high aspect ratio walls of width 60 and 120 nm. The structures were written with a 1 MeV proton beam.

This contrasts with three-dimensional (3D) lithography using penetrating electromagnetic radiation (e.g., x rays) which exhibits an exponential dose distribution with depth. (d) Reduced proximity effects. One big advantage of lithography with protons is the virtual absence of high energy secondary electrons which can give rise to unwanted exposure of resist in e-beam lithography. In e-beam writing, much of the energy is dissipated in the form of secondary electrons with an energy of 2–50 eV, with a small but significant fraction of the secondary electrons having significant energies which can contribute to the proximity effect in the range of a few tenths of microns.[8]

The use of proton beams for creating sub-100 nm structures has been achieved with the construction of a custom-made p-beam writing facility based around a focusing system consisting of a triplet of high demagnification quadrupole lenses (OM52), coupled with a state-of-the-art, high brightness, 3.5 MV single-ended accelerator (HVEE Singletron). The Singletron accelerator produces proton beams of much higher energy stability[9,10] than the more common belt-driven Van de Graaff accelerator, and the focusing system has performances achieving proton beam spot sizes of $35\times75\,nm^2$ for MeV protons.[11] The sample is mounted on a computer controlled Burleigh Inchworm XYZ stage which has a travel of 25 mm for all axes with a 20 nm closed loop resolution. The system has been designed to be compatible with Si wafers up to 6 in. The beam can be scanned with a set of magnetic scan coils over the sample or stage scanning can be employed. Since both methods are relatively slow we are currently installing a faster electrostatic scanning system to allow us to reduce exposure times 1–2 orders of magnitude. The scanning software for p-beam writing has been developed in-house.[12] Here we report technology demonstrations of the p-beam writing technique for producing high resolution 3D structures in SU-8 and PMMA at the 100 nm level and below.

A focused 2 MeV proton beam was written in a matrix of square shapes into a 10-μm-thick film of SU-8 resist spin coated onto a silicon wafer (Fig. 1). The squares have vertical side walls and have very smooth side walls. Atomic force microscopy (AFM) on similar structures show a rms sidewall roughness of 2.5 nm as predicted by calculations using SRIM[1] coupled with the limited range of the delta rays. To determine the nanolithographic capability of our p-beam writing facility, test structures were written using a 1 MeV proton beam in a 10-μm-thick layer of SU-8 negative resist, spin coated onto a Si wafer. In this experiment 1 MeV protons were focussed down to a spot size of $60\times120\,nm^2$ and scanned in a square pattern into a thick SU-8 film (Fig. 2 inset). The sidewalls appear rougher than in Fig. 1. This is sometimes seen in the more sensitive SU-8. More research is needed to eliminate the cause of this; currently the most likely reasons are thought to be beam intensity fluctuation or the quality of the SU-8. During the exposure, extra lines were written through the center of the squares forming a high aspect ratio nanogrid. As can be seen in the scanning electron micrograph (SEM) pictures in Fig. 2, the single written lines are 60 and 120 nm in width, which we believe is currently the smallest written single line in SU-8.[13,14] The support given by the adjacent square pillars ensures that the structural integrity of the narrow wall is not degraded during the development procedures. The narrow wall structure exhibits an aspect ratio of more than 160. Only Bogdanov and

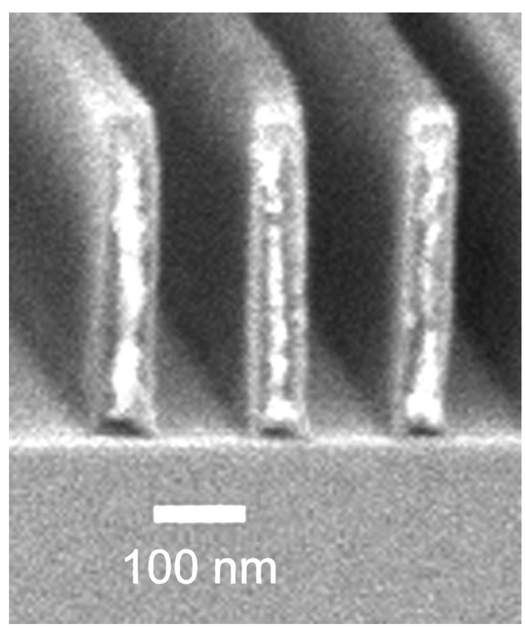

FIG. 3. SEM image of parallel lines written in a 350-nm-thick PMMA layer. The structure was written with a focused 2 MeV proton beam. The photo indicates a wall width of 50 nm.

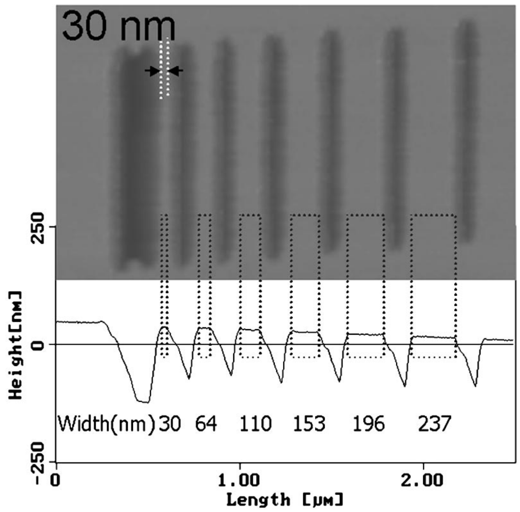

FIG. 4. AFM image of parallel lines written in a 200-nm-thick PMMA layer, including a line scan indicating a smallest linewidth of 30 nm. The structures were written with a 1 MeV proton beam.

Peredkov[13] have reported similar aspect ratios for SU-8 structures, but with a structural width of 4 μm or more.

Parallel grooves and lines were written within an area $20\times 20\ \mu m^2$ in a 350-nm-thick PMMA film spincoated on Si. Since imaging of sub-100 nm structures in polymer films requires special sample preparation, these structures were written parallel with the edge of the sample and 30 μm from the edge. Using a precision diamond scriber/breaker we cleaved the Si along a crystal plane which encompassed the line structures, allowing us to image the cross sectional profile. The high aspect ratio walls, estimated to be 50 nm wide, are shown in Fig. 3.

A further series of variable width parallel lines have also been written in 200-nm-thick PMMA, again spin coated on to a Si wafer. Due to the inherent difficulties in SEM sample preparation of PMMA structures below 50 nm, an AFM was used to image the structures. Figure 4 shows an AFM image of the narrowest lines obtained in the thin PMMA layer, together with a line scan perpendicular to these lines. The AFM image and line scan indicate a minimum line feature size of 30 nm coupled with an edge smoothness of less than 3 nm.

Although the technique of p-beam writing is still in its infancy, the technique shows great potential for 3D direct writing, particularly in the sub-100 nm range. The performance of p-beam writing is dependent on how well we can focus MeV protons, and through recent advances in proton beam focusing we can now achieve proton spot dimensions down to the 35 nm level.[11] There is no scientific reason why this performance should not be improved, and due to the reduced proximity effects compared with the highly successful e-beam writing, p-beam writing offers a powerful method for producing 3D nanostructures.

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