Nanoscale fabrication using single-ion impacts

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ABSTRACT

We describe a novel technique for the fabrication of nanoscale structures, based on the development of localized chemical modification caused in a PMMA resist by the implantation of single ions. The implantation of 4 MeV He ions through a thin layer of PMMA into an underlying silicon substrate causes latent damage in the resist. On development of the resist we demonstrate the formation within the PMMA layer of clearly defined etched holes, of typical diameter 30 nm, observed using an atomic force microscope employing a carbon nanotube SPM probe in intermittent-contact mode. This technique has significant potential applications. Used purely to register the passage of an ion, it may be a useful verification of the impact sites in an ion-beam modification process operating at the single-ion level. Furthermore, making use of the hole in the PMMA layer to perform subsequent fabrication steps, it may be applied to the fabrication of self-aligned structures in which surface features are fabricated directly above regions of an underlying substrate that are locally doped by the implanted ion. Our primary interest in single-ion resists relates to the development of a solid-state quantum computer based on an array of 31P atoms (which act as qubits) embedded with nanoscale precision in a silicon matrix. One proposal for the fabrication of such an array is by phosphorous-ion implantation. A single-ion resist would permit an accurate verification of 31P implantation sites. Subsequent metalisation of the latent damage may allow the fabrication of self-aligned metal gates above buried phosphorous atoms.


Keywords: Silicon quantum computer, ion implantation, PMMA, AFM, carbon nanotube

1. INTRODUCTION

The lateral dimensions of microelectronic components have been reduced systematically by a factor of two every six years, as formulated in Moore’s law. Current devices, which require a minimum feature size of about 200 nm, make use of extensively developed conventional lithographic techniques. Continued miniaturization, beyond the next decade, will become difficult, requiring the development of new technologies that can operate with adequate throughput at the nanoscale level. However, such an evolution would offer not only the miniaturization of conventional microelectronic circuits, but also the potential of new devices based on quantum operation. Our primary interest relates to the development of a solid-state nuclear spin quantum computer, proposed by Kane, which is based on an array of 31P dopants (which act as qubits) embedded with nanoscale precision in a silicon matrix. The device has a MOS-type structure with single 31P donor atoms buried, at a depth of order 20 nm, within a Si substrate. Quantum logic operations are controlled by the application of appropriate electrostatic potentials via a set of metallic gates, separated from the silicon substrate by a SiO2 layer. Fabrication of such a device relies on an ability to construct metallic gates of dimension ~10 nm on the surface in the vicinity of individual 31P dopants. The implantation of 31P ions is proposed as a possible route to fabrication of a Kane device. Here we explore the possibility of implanting the 31P ions through a thin film resist both to register the passage of each individual ion, and furthermore allow the fabrication of self-aligned control gates by subsequent metallisation.
Ion irradiation is an established tool for modification of the chemical structure and physical properties of materials, and it has been shown that material properties can be modified in a controlled way by changing the ion-beam fluence. The effect of ion-beam irradiation on thin film resist materials is of interest to us here, particularly those resists which may have sufficient sensitivity to demonstrate a measurable modification due to the passage of a single ion. Several materials have been studied as candidates for a single-ion thin film resist, including diamond-like carbon, polymethylmethacrylate (PMMA), monolayer films of C60 and self-assembled monolayers of Cyclooctatetraene. Studies tend to be restricted either to the use of high-energy heavy ions, or require particular environmental conditions, such as ultra-high vacuum. A versatile resist material which is sufficiently sensitive to demonstrate chemical modification induced by the impact of single low-energy ions, and which permits subsequent metalisation would be a very useful tool in the future development of nanoscale devices.

In this paper we explore further the use of PMMA as a single-ion resist, specifically for application to the fabrication of the Kane quantum computer. Previous studies of single-ion irradiation of PMMA examined surface tracks induced by 20 MeV Au impacts, caused by the direct mechanical modification (plastic deformation) of the film at the impact sites. Here we are concerned with 31P ions of low energy (~ 15 keV), where modification to the PMMA layer takes the form of latent chemical damage caused by secondary electron emission arising from electronic stopping of the passing ion, which is revealed by subsequent development of the irradiated sites. The preliminary experiments presented here make use of 4He ions, of energy 4.0 MeV; for reasons that we shall address, these afford an accurate model for the use of low energy 31P ions. In section 2 we outline the irradiation and processing of PMMA thin film samples. We make use of AFM imaging in intermittent-contact mode, in section 3, to examine the surface topography of irradiated films. The identification of single-ion impact sites requires Atomic Force Microscopy (AFM) imaging of not only high spatial resolution, but also the ability to image high aspect-ratio structures. In section 4 we employ carbon nanotube scanning probes to identify craters in the PMMA films induced by single-ion impacts. We discuss the implementation of subsequent metalisation to form contacts to the locally doped regions of the substrate in section 5.

2. PMMA FILM IRRADIATION AND PROCESSING

A 31P ion implanted into a material will suffer both electronic energy loss, giving rise to secondary electrons, and nuclear energy loss, sufficient to create defects. Nuclear energy loss predominantly occurs close to the end of the implanted-ion path; presumably the extent of nuclear energy loss in a thin PMMA resist layer will be minimal, and its effects need not concern us here. The experiments presented here make use of 4.0 MeV 4He ions, which suffer very little nuclear stopping and have an electronic energy loss, of about 11eV/Å, that is comparable to that of 15 keV 31P ions. We therefore suppose that chemical modification of the PMMA resist resulting from irradiation with 4He ions is a good model for modification suffered under 31P ion implantation.

PMMA thin films, of thickness about 50 nm, were prepared by spin-coating onto native silicon wafers. 4He irradiation was carried out, at normal incidence, using the University of Melbourne 5U Pelletron. Each sample was irradiated at room temperature with an array of spots, of diameter 0.7 mm, with varying ion fluence, from 10⁹ to 10¹⁴ ions.cm⁻². The pressure in the implantation chamber was around 10⁻³ torr. Samples were subsequently developed by chemical etching in a solution of MIBK:IPA (1:3), carried out for a time of 90 s, to maximize the size of the etched features for subsequent AFM imaging.
3. AFM IMAGING

The surface topography of the irradiated films was analysed by atomic force microscopy in air using a JEOL 4200SPM. Optical micrographs of the PMMA films following etching revealed significant non-uniformity in the ion fluence across each irradiated spot, making it difficult to gain a quantitative measure of the ion fluence in each case. However, examination of the surface topography along a profile across each irradiated spot is sufficient to demonstrate the effect of varying ion fluence on the structure of the PMMA thin film.

Initial AFM images were obtained using Si cantilevers (with probes of nominal radius of curvature < 35 nm and cone angle < 20°). Imaging was carried out in intermittent-contact mode to minimise damage to the PMMA films; repeated observation of a scanned area illustrated no unintentional surface modification arising from AFM imaging. Fig. 1 shows a series of AFM images, of scan area 1×1 µm, obtained at various locations from the centre, to the edge of a single spot, irradiated with a mean ion fluence of 1.8 x 10^13 ions.cm^-2. At the centre of the irradiated area, near complete etching of the PMMA film on development is observed, arising from a high ion fluence. As we scan towards the edge of the irradiated area it is possible to resolve pits of irregular shape in the surface topography, of dimension 100-200 nm, corresponding presumably to chemical modification arising in the PMMA film from many closely spaced ion impacts. Close to the edge of the irradiated area, indentations of dimension ~35 nm can be observed. These features may arise from etching of single-ion impact sites, but it is not possible to resolve individual etched holes. AFM imaging in this manner therefore does not permit determination of the size of etched features induced by single-ion impacts.

Figure 1: Intermittent-contact AFM images (1×1 µm), obtained using a conventional Si cantilever, showing the effect on PMMA thin film topography of 4He irradiation at varying ion fluence: High fluence (top-left image) to low fluence (bottom-right image).

The difficulty in observing single-ion etched features derives from characteristics of the cantilevers employed for AFM imaging, the shape of the probe determining both the lateral resolution and capability for imaging features of high aspect ratio. Conventional Si cantilevers, while presenting reasonable lateral resolution (~35 nm) on moderately flat surfaces, are unsatisfactory when applied to rough surfaces with steep and deep features. The effect on AFM imaging of this limit in resolution, applied to the analysis of the 4He-irradiated PMMA films is illustrated in Fig. 2, which shows a region of PMMA irradiated with an ion fluence ~10^9 ions.cm^-2. The topographic profile (Fig. 2b) of an individual etched feature, of dimension comparable to the radius of curvature of the probe, is seen to reflect the shape of the probe and not that of the feature under study. In Fig. 2 it is apparent that use of a conventional Si cantilever does not permit us to accurately image the base of the pits etched in the PMMA film. We must therefore look to an alternative method of imaging.
4. CARBON-NANOTUBE AFM IMAGING

The fabrication of scanning probes using carbon nanotubes has been an area of increasing promise during recent years. Probes consisting of multi-walled nanotubes have been fabricated by mechanically attaching either a bundle or a single nanotube to a conventional silicon probe using an adhesive\(^{11}\) or an electrostatic technique\(^{12}\). Single-walled nanotube probes have been fabricated by direct growth onto a silicon probe by chemical vapour deposition\(^{13}\), a technique offering a more practical route to mass production. The geometry of a carbon nanotube, with intrinsic diameter as small as 0.7 nm for single-walled tubes, and length up to several microns, offers extremely good lateral resolution in imaging features of very high aspect ratio\(^{14}\), compared to a conventional cantilever (Fig. 3). The probing of individual holes etched in PMMA films is a natural task for such a scanning probe.

Figure 2: a) Intermittent-contact AFM image (1×1 µm), obtained using a conventional Si cantilever, showing a region of PMMA irradiated with an ion fluence of ~10\(^7\) ions.cm\(^{-2}\). b) topographic profile taken from an individual etched feature (shown in 2a)).

Figure 3: SEM image of a multi-wall carbon nanotube probe. Courtesy of Piezomax Technologies, Inc\(^{15}\).
We make use of Piezomax\textsuperscript{15} carbon nanotube probes. The specific probes employed consist of multi-walled carbon nanotubes, of diameter about 10 nm and length 500 nm, attached to conventional DI TESP Si cantilevers. A typical topographic image of an irradiated PMMA film, obtained by AFM in intermittent-contact mode, employing a carbon nanotube probe, is illustrated in Fig. 4. The image corresponds to a region of PMMA irradiated with \(^{4}\text{He}\) ions with ion fluence \(\sim 10^{9}\) ions.cm\(^{-2}\), and is seen to reveal a large number of individual etched features of sub-50 nm dimension. The larger features appear to be rather irregular in shape, and may result from the combined latent damage resulting from a small number of closely spaced impact sites. Smaller features tend to be more regular in shape, roughly circular, as would be expected for etching of a single-ion impact. The total number of features is of the same order as the estimated ion fluence for that region of the sample.

![Image](image_url)

Figure 4: a) Intermittent-contact AFM image (1×1 µm), obtained using a carbon nanotube probe, showing a region of PMMA irradiated with an ion fluence of \(\sim 10^{7}\) ions.cm\(^{-2}\). b) Topographic profile taken from an individual etched feature (shown in 4a)).

The improvement to lateral resolution of imaging with the nanotube probe is clearly demonstrated in Fig. 4b, which shows a topographic profile across an individual etched hole. This profile indicates structure at the bottom of the etched hole, which has a depth of about 30 nm. Measurement of topographic profiles for the other etched features in this image indicate holes of similar depth; presumably the discrepancy between the film thickness prior to irradiation and the film thickness observed by profiles is due to the large development time. That is unirradiated PMMA will still etch if the development time is sufficiently long.

The lateral dimension of the smallest hole observed in Fig. 4 is about 12.5 nm, close to the expected lateral resolution of the nanotube probe. We believe that the smallest features observed are likely to be a result of the latent damage induced in the PMMA film by the impact of a single implanted \(^{4}\text{He}\) ion.

5. METALISATION TO FORM SELF-ALIGNED CONTACTS

We have established that PMMA has adequate sensitivity to ion irradiation at the single-ion level, to permit its use as a resist to register the passage of individual implanted ions. Single ion features in the PMMA films, formed by subsequent etching, take the form of near-circular holes of lateral dimension \(~12\) nm. Subsequent metalisation of the developed films would perhaps allow us to form self-aligned contacts above regions of the underlying substrate that are locally doped with a single implanted ion, as required in the Kane device. Enabling the connection of contacts formed in this way to external circuitry would perhaps be a difficult task. However, focused ion beam technology is now sufficiently developed that metallic features, of minimum dimension \(~20\) nm, can be written directly on a surface\textsuperscript{16}. It may be possible, therefore to implant ions into a device with pre-fabricated external contacts, and to use FIB-based technology to
make connections to self-aligned contacts formed by metalisation of single-ion etched holes. Scaling to a device consisting of many such connections would remain a difficult task.

6. CONCLUSION

AFM imaging clearly shows the material properties of PMMA can be modified in a controlled way by changing the ion-beam fluence. PMMA appears to have adequate sensitivity to ion irradiation at the single-ion level to permit its use as a resist to register the passage of individual implanted ions. The identification of ion paths is simplified greatly by nanotube probes improving the lateral resolution of AFM images. We envisage that PMMA will allow us to subsequently metalise the developed films allowing us to form self-aligned contacts above regions of the underlying substrate that are locally doped with a single implanted ion, as required in the Kane device.

REFERENCES


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