Nuclear Instruments and Methods in Physics Research B 269 (2011) 2409–2412

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Exposure parameters in proton beam writing for KMPR and EPO Core negative tone photoresists

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ARTICLE INFO

Article history:
Available online 26 February 2011

ABSTRACT

In spite of its recent establishment, proton beam writing (PBW) has already demonstrated to be a highly competitive lithographic technique. PBW is a fast direct-write technique capable of producing high-aspect-ratio micro- and nano-structures in resist material. Typical applications can be found in nanoimprinting, biomedical research, photonics, and optics, among other fields. The progress of PBW is linked to the successful introduction of new resist materials. In this paper, KMPR and EPO Core, negative tone photoresists are tested on their compatibility with PBW. KMPR resist has similar chemical and process properties compared to SU-8. Employing UV lithography on KMPR resist, details of 30 μm have been obtained in Ni, indicating a possible advantage compared to SU-8 for optical lithography [1]. In this study, the sensitivity to MeV proton exposure and sub-micron feature sizes are presented in KMPR. PBW has been also combined with Ni electroplating in order to determine the suitability of KMPR and EPO Core resist to fabricate 3D metallic moulds and stamps.

1. Introduction

Proton beam writing (PBW) is a direct-write technique that uses a highly focused beam of MeV protons to pattern structures in a suitable resist material at micro- and nanodimensions. Protons compared to other kinds of radiation like electrons, UV light and X-rays offer some interesting and unique advantages [2]. Because of the huge mass difference between protons and electrons there is little energy transfer between the incoming proton and individual substrate electrons. This results in a deep and straight proton track into the resist material, a short range of the secondary electrons and therefore minimal proximity effects. These characteristics enable PBW to fabricate three-dimensional, high aspect ratio structures with vertical, smooth sidewalls and low line-edge roughness. The technique can be applied to produce arbitrary structures in different materials with applications in optics (e.g. waveguides, laser arrays and gratings) [3,4] and biology (micro-fluidic devices, biostructures and biochips) [5,6]. PBW can also perform machining of multilayers to form piled microstructures [7–9] and Si modifications including fabrication of Si microstructures [10] and porous Si patterning [11] applying different beam energies and exposure fluences.

Since the development of PBW by Prof. Frank Watt's group at the Centre for Ion Beam Applications (CIBA), National University of Singapore, in 1997 [12], a variety of materials has been tested, however the compatibility with PBW has only been found for a few of them [13–18]. The low cost, simple processing steps, optical and mechanical characteristics, resistance to chemicals, and biocompatibility make polymers an attractive alternative compared to glass and Si for microsystem technologies [19,20]. There are several resists which have shown nano-structuring capabilities using PBW. Polymethylmethacrylate (PMMA) is until now the most popular polymer resist used in PBW, other materials with nano-structuring capabilities are hydrogen silesquioxane (HSQ) and SU-8 (a chemically amplified epoxy based resist). However, the removal of SU-8 after electroplating remains a challenge. SU-8 is very difficult to be stripped after electroplating, especially when the structures are small. Other resists like ma-N 440, a negative resist under proton beam exposures, can be easily stripped after electroplating [21].

In this paper, the behavior of KMPR (Microchem) photoresist is studied after its irradiation with a proton beam in order to determine the suitability of this resist for PBW applications. The sensitivity and the lateral resolution of this resist for PBW using the CIBA nanoprobe facility were investigated. KMPR is a chemically amplified negative tone epoxy based resist. Its similar lithographic properties to SU-8 have allowed to adapt it successfully for high-aspect-ratio UV lithography and electroplating applications [1]. EPO Core (Micro Resist Technology) was also tested in combination

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doi:10.1016/j.nimb.2011.02.027

with PBW. This is also a negative tone photoresist which is often used for the fabrication of waveguides [22].

2. Experimental

The process starts with preparation of a Si substrate. The Si wafer was coated with a 20 nm thick Cr layer and 40 nm thick Au layer using magnetron sputter deposition (Nanofilm Technologies International Pte. Ltd.). The coated metals were used as conductive seed layer for the Ni electroplating. The KMPR used in this study with PBW was KMPR 1005 which is designed to yield 5 to 10 μm thick layers in a single spin coating step. More process details can be found from the MCC KMPR datasheet [23]. In this experiment, the spin coating was conducted at 4000 rpm for 30 s. Next, the wafer was baked on a hotplate at 100 °C for 5 min. Applying longer baking times resulted in cross-linking of the KMPR resist. The final KMPR layer was 7.6 μm thick.

EPO Core was coated on a Si wafer which was prepared with a Cr/Au seed layer for electroplating. Here, the spin coating was conducted at 1500 rpm for 60 s. After the spin coating, the wafer was baked on a hotplate at 50 °C for 10 min and then at 85 °C for 12 min. The final layer obtained was 42 μm thick.

The samples were exposed with a beam of 2 MeV protons focused to a square spot of about 200×200 nm^2 through magnetic quadrupole lenses in the PBW line at the Centre for Ion Beam Applications (CIBA) in the Physics Department of the National University of Singapore [24,25]. Sets of parallel lines featuring 750 nm up to 10 μm in width were written by the beam in a layer of 7.6 μm thick KMPR resist. The fluence was varied from 1.9×10^{11} to 3.1×10^{14} protons/cm^2. In the case of EPO Core, sets of squares of 10×10 μm^2 were written with a fluence ranging from 6.3×10^{9} to 3.1×10^{14} protons/cm^2.

After the exposure, all KMPR coated wafers were developed in a 2.38% tetramethyl ammonium hydroxide (TMAH) solution for 5 min followed by a DI water rinse. The samples were dried using N_2 gas. Development delay effects were investigated; some samples were developed immediately after the PBW, another group of samples one week later and a final set of samples two weeks after the irradiation. Some wafers were baked at 100 °C for 3 min. before the development whereas others wafers were developed without baking. As a direct comparison to earlier work [21], standard UV lithography at 365 nm was performed on KMPR resist using an Oriel contact printing system. The thickness of the KMPR pattern on the substrate was measured by scanning electron microscopy (SEM).

The EPO Core coated wafers were developed immediately after exposure in mr-Dev 600 (Micro Resist Technology) for 3 min followed by a DI water rinse. Then the samples were dried in air.

Nickel electroplating was performed using a nickel plating machine (Technotrans AG, RD. 50), installed in the class 1000 CIBA clean room (1000 P/ft^3). After electroplating, KMPR was stripped by immersing the samples in either Nano Remover PG (MicroChem) at 80 °C or Remover K (MicroChem). For the removal of finer details also ultrasonic agitation was employed.

3. Results and discussion

For the KMPR coated wafers, the quality is best for the lines developed immediately after the exposure as observed in optical microscopy. The stability of the lines developed 14 days after exposure was very poor. Directly after development the lines were almost vertical and straight, when observing the lines two weeks later they had become very wavy. For the wafers developed immediately after the exposure, the post-exposure bake results in a reduced fluence required for cross-linking (see Fig. 1). For the

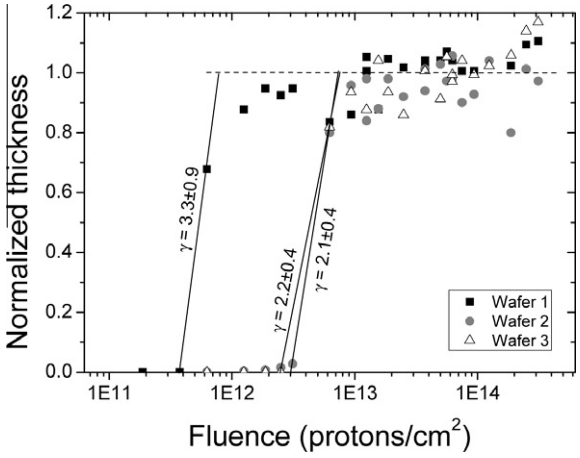

Fig. 1. Contrast curves for wafer 1, 2 and 3 for 2 MeV proton exposure. Wafer 1 was baked and developed immediately after exposure, wafer 2 was developed immediately after exposure without any post-exposure bake and wafer 3 was developed one week after, again without any post-exposure bake. The thickness is normalized to one for a fully cross-linked resist.

wafers developed one week later, the baking did not seem to have any effect on either the sensitivity or contrast. In order to compare the different wafers directly, all the thicknesses were normalized to 1 for fully cross-linked resist, and the contrast curves for wafers 1, 2 and 3 were obtained (Fig 1). Wafer 1 corresponds to the wafer which was baked and developed immediately after the exposure, wafer 2 was developed immediately after the exposure without any post-exposure bake and wafer 3 was developed one week after the exposure, again without any post-exposure bake. Typical structures obtained for these measurements are shown in Fig. 2a, featuring 10×50 μm^2 lines (wafer 1). Exposing wafer 3 with 2.8×10^{13} protons/cm^2 resulted in 750 nm wide lines, see Fig. 2b, this corresponds to an aspect ratio (height/width) of 10. The lines are not very straight, either due the high aspect ratio and or insufficient cross-linking, further study is required to optimize sub-micron structuring of KMPR resist using MeV proton beams. Wafers baked and developed one week after the exposure showed a similar behaviour as wafer 3 (not shown in Fig. 1). The contrast of the samples is calculated here as $\gamma = 1/[\log(\Phi_f) - \log(\Phi_i)]$ where Φ_f is the fluence at which the resist is fully insoluble and Φ_i the fluence where the resist becomes insoluble for the developer and was found to be 2–3. The sensitivity or Φ_f is the minimum required proton fluence for fully cross-linked structures. Typical values of Φ_i and Φ_f mark where the contrast curve starts to deviate from zero and reaches full resist thickness, respectively. The exact values are extrapolated through a straight line as shown in Fig. 1. The sensitivity was 7.5×10^{11}, 7.2×10^{12} and 7.5×10^{12} protons/cm^2, for wafer 1, 2 and 3, respectively. We can conclude that the best resist performance is obtained with wafer 1, i.e. post-exposure bake and development directly after PBW.

In the case of EPO Core, a contrast of 0.9 ± 0.3 was obtained. It must be noted that the relatively large error is due to the fact that at lower fluences the partially cross-linked structures get detached from the surface. The sensitivity was about 6.3×10^{11} protons/cm^2.

HSQ has a limited functional lifetime and it presents a wide contrast range (2–8) [26,27]. It has a sensitivity ranging from 1.9×10^{13}–1.3×10^{14} protons/cm^2 depending on the batch used which makes it difficult to work with, because one needs to calibrate every time a new batch is used. Furthermore, the SU-8 sensitivities are similar with 1.9×10^{13} protons/cm^2. This makes KMPR and EPO Core attractive resists which can be structured relatively quickly. The contrast of PMMA does not degrade as the resist ages, its value is higher (5–6) [28] than that of KMPR which means that

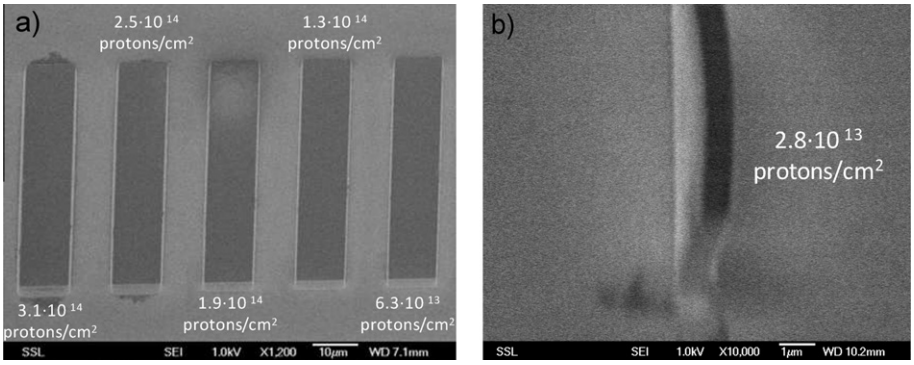

Fig. 2. (a) SEM image of $10 \times 50\ \mu m^2$ lines written in KMPR with a 2 MeV proton beam. The fluences ranged from 6.3×10^{13} to 3.1×10^{14} protons/cm^2 from left to right. The sample was baked and developed immediately after exposure (wafer 1). (b) SEM image of 750 nm wide line fabricated using 2.8×10^{13} protons/cm^2. The sample was developed one week after exposure without any post-exposure bake (wafer 3).

the structures written in PMMA can be straighter and support higher density structures.

Lines of $1 \times 100\ \mu m^2$ were written in KMPR using a relatively high fluence (more than 6.3×10^{13} protons/cm^2) in order to guarantee structural integrity during development and the following Ni electroplating process (see Fig. 3a). For the test sample shown in Fig. 3b, the KMPR resist could not be removed completely after Ni plating without compromising the Ni mould structure. By employing the remover K from MicroChem the KMPR resist can be completely removed but the removal process has a detrimental influence on structural quality of the Ni mould as shown in Fig. 3b. Structures with features sizes below 10 μm could not be removed with the Nano RemoverPG. Here, similar results were obtained for KMPR exposed using standard UV lithography.

In the case of EPO Core, squares were exposed with a fluence of 1.3×10^{12} to 1.9×10^{12} protons/cm^2 using 2 MeV protons. Here, relatively smooth pillars (see the left two squares in Fig. 4), featuring an aspect ratio of 4 were obtained. Incomplete cross-linking is observed at a fluence of 6.3×10^{11} protons/cm^2, as can be seen in the centre of each of the right two squares in Fig. 4.

The EPO Core resist could not be removed after Ni electroplating. Here, the EPO Core sample was immersed in acetone with ultrasonic agitation for 1 h as well as 12 h, but no change could be observed on the resist layer.

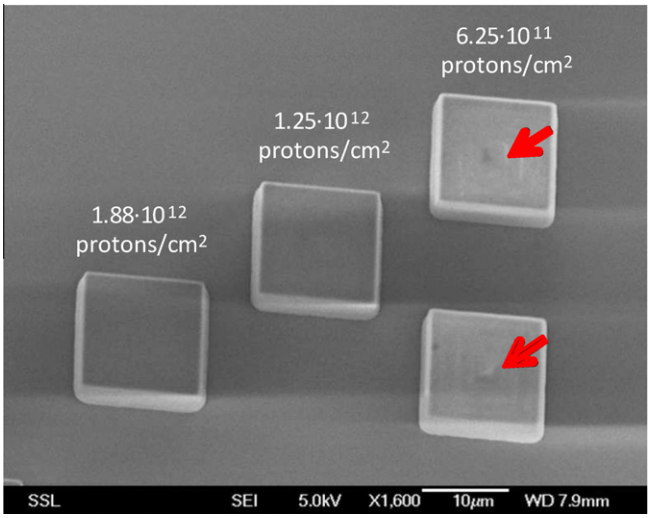

Fig. 4. SEM image of EPO Core squares written with a 2 MeV proton beam exposed with 6.3×10^{11} (right squares), 1.3×10^{12} and 1.9×10^{12} protons/cm^2 (left squares). The arrows point to the centre region where insufficient cross-linking was observed.

4. Conclusions

We have demonstrated that KMPR and EPO Core are potentially useful negative tone resists for PBW. Structures down to 750 nm have been obtained in KMPR resist featuring an aspect ratio of 10. A sensitivity of about 6.3×10^{12} protons/cm^2 and a contrast of 2–3 were observed for 2 MeV protons cross-linking the negative resist KMPR. The best results are obtained applying a post–exposure bake followed by development directly after proton beam writing. In the case of EPO Core a sensitivity of 6.3×10^{11} protons/cm^2 and a contrast of 0.9 ± 0.3 were observed for 2 MeV

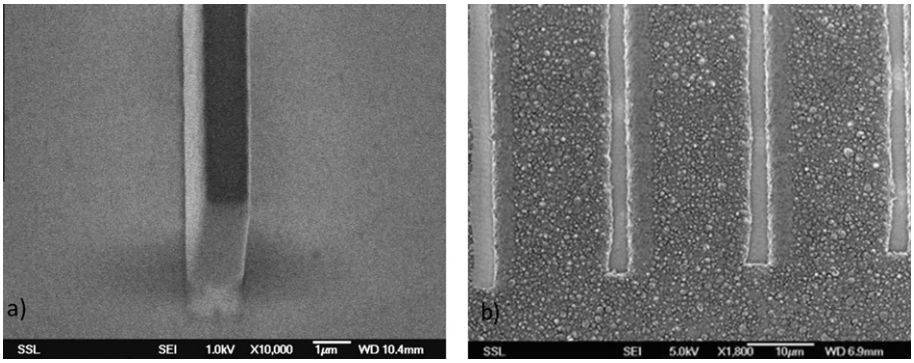

Fig. 3. (a) SEM images of $1 \times 100\ \mu m^2$ lines written in KMPR using a 2 MeV proton beam with 8.8×10^{13} protons/cm^2. The sample was developed one week after the exposure. (b) SEM images of $1 \times 100\ \mu m^2$ lines in Ni after the KMPR removal with the Remover K (MicroChem).

proton beam exposure. The EPO Core resist could not be removed after Ni electroplating. An aspect ratio of 4 was observed in the case of PBW in EPO Core. The removal of the KMPR resist was not successful for fine features smaller than 10 μm after Ni electroplating. This was observed for both KMPR exposed with MeV protons as well as standard UV lithography at 365 nm.

Acknowledgments

The research of the first author was supported by the program Jose Castillejo of the Spanish Ministerio de Educación y Ciencia. We also acknowledge the support from A-Star Singapore (R-144-000-261-305).

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