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New resists for proton beam writing

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Abstract

To explore the full capabilities of proton beam writing (PBW) as a lithographic tool it is important to investigate potential new resist materials. In PBW the interactions of the protons with the resist are comparable to the electron interactions with the resist in electron beam writing. In both techniques the induced secondary electrons will modify the molecular structure of the resist, therefore electron beam resists are potential candidates for PBW.

Here we discuss resist properties such as contrast and sensitivity of two new negative resists for PBW. The first resist is a spin-coatable TiO_2 resist for which sub 10 nm resolution has been reported using electron beam writing. In PBW smooth side walls have been observed for this resist. Despite a relative low sensitivity of this resist for PBW (8000 nC/mm^2) it has potential applications in the area of integrated optical components such as waveguides and gratings because of its high refractive index. WL-7154 is a UV-sensitive negative resist and shows high sensitivity for PBW (4 nC/mm^2). This resist could function as a mold for Ni electroplating to fabricate Ni stamps for nano-imprint- and soft-lithography.

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Keywords: Proton beam writing; Direct write; High aspect ratio; Resist

1. Introduction

To expand the applications of PBW it is important to investigate potential new resists. Until now the only resists compatible with PBW which have demonstrated sub-100 nm features are PMMA and SU-8 [1], although recently HSQ has also demonstrated sub-100 nm features [2]. Other resists such as PMGI [3], DiaPlate 133 [4] and ADEPR [5] have also been investigated for their effectiveness in combination with PBW. In Table 1 a summary of resists compatible with PBW is presented. In p-beam writing the dose required is typically 100 times lower compared with sensitivities reported in e-beam writing for different resists [6–8].

Titanium dioxide has shown its potential application in solar cells [16,17], optical waveguides [18–20], gas sensors [21] and electrochromic displays [22,23]. One of the hindrances for miniaturization of these devices is the lack of an easy and reliable way of patterning TiO_2. Conventionally, TiO_2 is patterned by sputtering it on to a prepatterned organic resist and then performing lift-off. The lift-off process however remains delicate, especially when complicated features and/or thick films of TiO_2 are desired, and it has been reported that successful casting of TiO_2 is limited to a maximum thickness of 150 nm [24]. To eliminate the problems associated with lift-off, we have tested a sol–gel-based spin-coatable TiO_2 resist for proton beam writing: this resist has already proved suitable for direct-writing

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Table 1
Current status and dose requirements in PBW

Resist	Type	Dose needed (nC/mm^2)	Smallest feature written
PMMA [3,9,10]	Positive	80–150	20–30 nm
SU-8 [1,3]	Negative	30	60 nm
HSQ [2]	Negative	30	22 nm
PMGI [3]	Positive	150	1.5 μm
WL-7154	Negative	4	800 nm
TiO_2	Negative	8000	5 μm
Si [11]	Negative	80,000	15 nm tip (implanted in channeling geometry)
DiaPlate 133 [4]	Negative	10	10 μm
ADEPR [5]	Negative	125–238	5 μm
Forturan [12]	Positive	1	3 μm
PADC (CR-39) [12,13]	Positive	600	5 μm
ma-N 440 [14]	Negative	200	400 nm
GaAs [15]	Negative	100,000	12 μm

using an electron beam down to the 10 nm [6]. Thick films can be easily patterned using PBW and this will be discussed here.

WL-7154 from Dow Corning is a photo-patternable spin-on silicone. This resist can be patterned using I-line (365 nm UV exposure). This resist can be applied in layers up to several microns. Here we discuss the functionality and processing parameters of WL-7154 as a proton beam resist.

2. Experimental procedures

The PBW has been performed at the Centre for Ion Beam Applications in the Physics Department of the National University of Singapore. A more detailed description of the set-up can be found elsewhere [1,25,26].

2.1. Investigations into the TiO_2 resist

The TiO_2 resist was produced as discussed by Saifullah et al. [6]. The viscosity of the resist was adjusted to achieve 7 μm thick layers while spinning for 120 s at 1500 rpm. After spinning, the wafers were placed in an oven after which the oven was switched on and heated to 75 °C. The sample was kept at this temperature for 10 h followed by natural cooling of the oven back to room temperature. Some cracks were observed after cooling the sample. During PBW efforts were made to avoid the cracked areas, but due to limited magnification of the optical visualization of the sample in the PBW exposure chamber not all the cracks could be avoided. Initial evaluation of the TiO_2 resist was performed using 1 MeV protons, and squares of $5 \times 5\ \mu m^2$ were written, as shown in Fig. 1(a). To further minimize the stress in the film, the squares were written in 1, 2, 3, 4 or 5 loops; in each loop a dose of 10,000 nC/mm^2 was used resulting in a final dose of 10,000 up to 50,000 nC/mm^2. After exposure, the sample was developed in acetone for 60 s followed by a rinse in DI water. As is clear from the SEM photo in Fig. 1(a), the square which received a dose of 30,000 nC/mm^2 is cracked. This is believed to be due to the residual stress in the film. To measure a contrast curve under similar experimental conditions as used for HSQ resist as described in [2], a 2 MeV beam was chosen to expose a similar pattern in the TiO_2 resist. The contrast is defined as $\gamma = 1/[\log(D_f) - \log(D_i)]$ where D_f is the dose at which the resist is fully insoluble and D_i the dose where the resist becomes insoluble. Here a dose ranging from 1800, 3600, 5400, 7200 and 9000 nC/mm^2 was used following the same exposure strategy as in the earlier experiment, i.e. in every loop 1800 nC/mm^2 was used. At 3600 nC/mm^2 the TiO_2 resist just received enough energy and a slight trace of TiO_2 is seen after development. D_i was therefore estimated to be 3000 nC/mm^2. At higher dose the squares are almost fully developed as can be seen

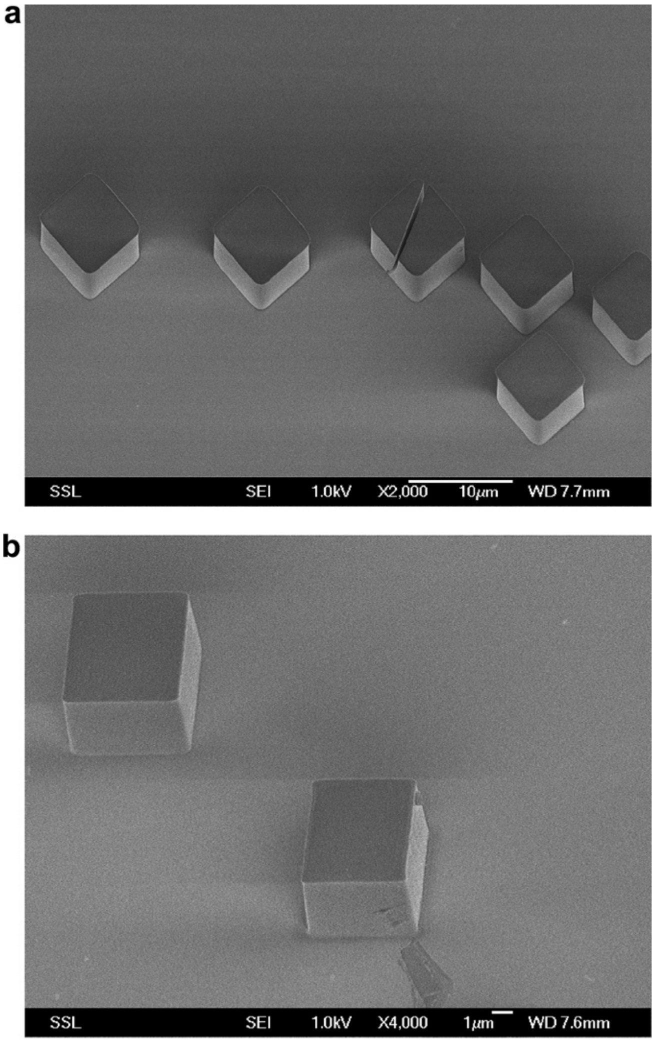

Fig. 1. SEM photo of $5 \times 5\ \mu m^2$ squares in TiO_2; (a) written with 1 MeV protons applying a dose ranging from 10,000 up to 50,000 nC/mm^2, (b) written with 2 MeV protons applying a dose of 5400 and 7200 nC/mm^2.

from Fig. 1(b). The squares in Fig. 1(b) received a dose of 7200 and 5400 nC/mm^2, located on the left and right side in the photo respectively. At a dose of 7200 nC/mm^2 the square is 6 μm high, at 9000 nC/mm^2 the square has reached 7 μm as measured from the SEM photo, this corresponds to the full height of the resist. D_f was therefore estimated to be 8000 nC/mm^2. A contrast of 2.3 (±0.5) can be extrapolated from the height obtained from SEM data. A weakness in the structuring of the TiO_2 using PBW appears to stem from underlying stress in the spin coated film. Further investigations to try and reduce the stress in the film were carried out. (a) A wafer was coated at 5000 rpm to achieve a thinner layer of TiO_2 followed by a bake at 40 °C, and (b) a second wafer was not baked after spincoating. Since both wafers still showed cracks in the TiO_2 layer, more tests are needed to produce better quality TiO_2 resist films.

2.2. Investigations into the WL-7154 resist

To test the functionality of WL-7154 resist for PBW, a layer was spun at 1500 rpm for 30 s to yield a thickness of 1.4 μm. The contrast and sensitivity of this resist were determined by writing squares of 10 × 10 μm^2 with 2 MeV protons with a dose varying from 1 up to 100 nC/mm^2. After exposure the structures are either baked at 100 °C for 15 s and developed in mesitylene for 60 s or directly developed in mesitylene for 60 s. There is no difference visible between these two procedures, therefore no post exposure bake was applied in the results presented here. Instead it was found to be beneficial to rinse the sample in DI water followed by a short rinse in fresh developer and again a rinse in DI water. The SEM photo in Fig. 2(a) shows two written squares which received a dose of 3 and 4 nC/mm^2. The square with the lowest dose did not fully crosslink resulting in a 53 nm thick layer of resist remaining after exposure and development, barely visible on the right hand side in Fig. 2(a). The point where the resist just becomes insoluble was therefore set at $D_i = 2.5$ nC/mm^2. At a dose of $D_f = 4$ nC/mm^2 or more the resist is fully insoluble in developer. In Fig. 2(b) squares with a dose of 5, 6, 7 and 8 nC/mm^2 are shown, the dose increasing from right to left. It appears that there is a residual thin film present which increases as the dose is increased. This residual film is caused by scattered beam as can be seen in between the squares in Fig. 2(b). Atomic force microscopy (AFM) measurements show that this film is typically less than 100 nm thick. By applying a second development step with fresh developer, a substantial part of this residual film can be removed. A contrast curve was measured with AFM and is shown in Fig. 3. Here a contrast of 6 ± 1 was found using the same definition as for the TiO_2 resist.

To test the production of small feature sizes in WL-7154 using PBW we exposed a 1.4 μm thick layer of WL-7154 resist by writing a grid pattern, digitized in a matrix of 4096 × 4096 pixels in a scan area of 100 × 100 μm^2. In order to achieve smooth side walls the pixel size was chosen much smaller than the beam size. A 2 MeV proton beam was focused down to 300 × 300 nm^2, as measured using a reso-

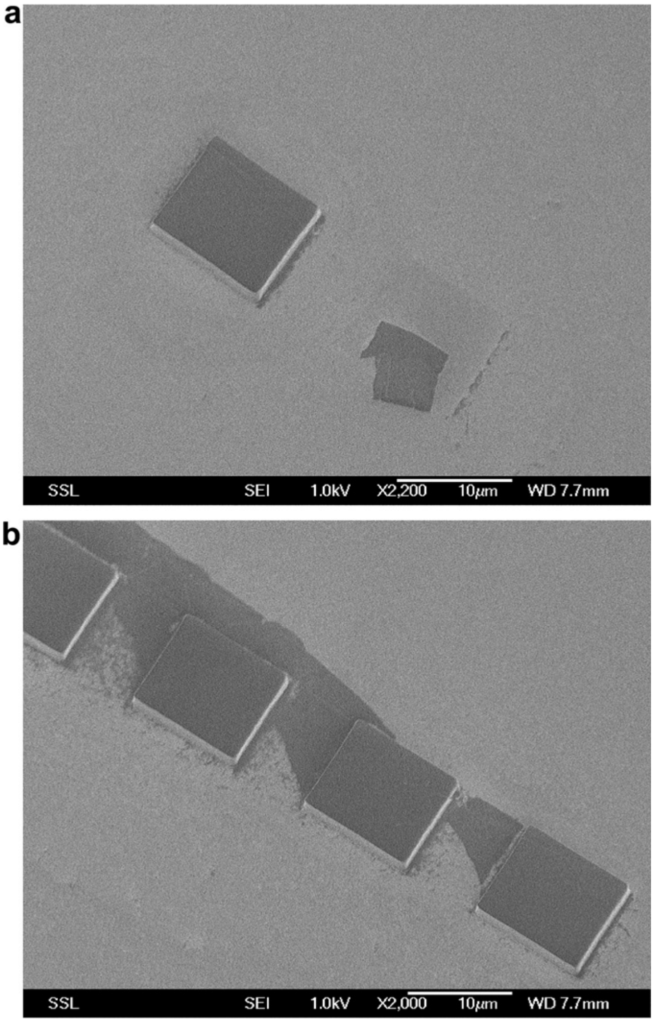

Fig. 2. SEM photo of 10 × 10 μm^2 squares in WL-7154 written with 2 MeV protons, in (a) a dose of 3 and 4 nC/mm^2 was used and in (b) a dose of 5, 6, 7 and 8 nC/mm^2 was used.

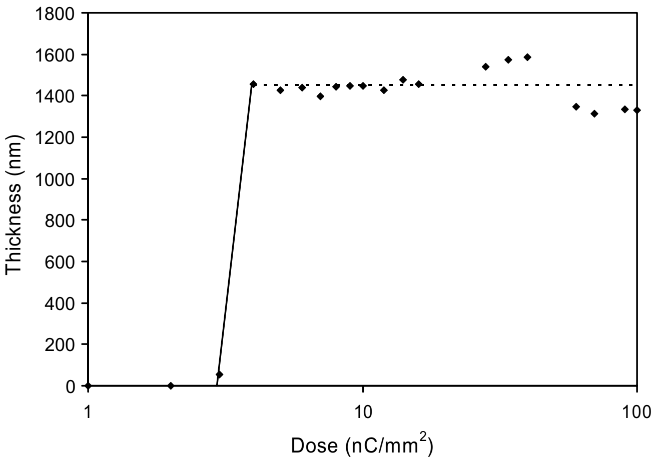

Fig. 3. Contrast curve of WL-7154 for 2 MeV proton beam exposure demonstrating a contrast of 6.

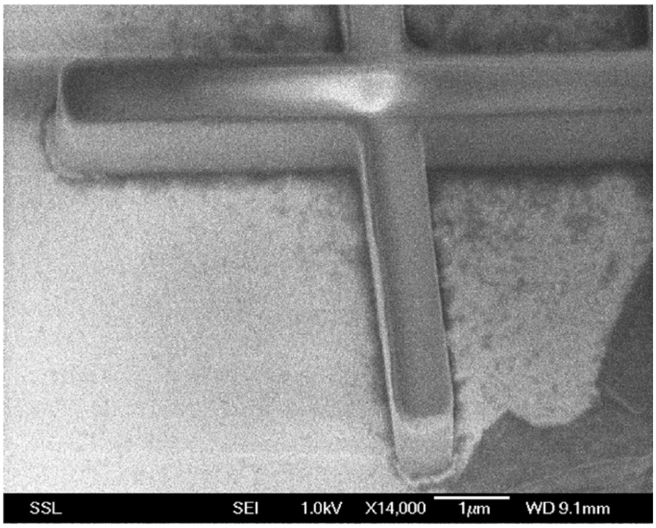

Fig. 4. SEM photo of sub-micron lines written in a 1.4 μm thick layer of WL-7154 using a 2 MeV proton beam focused down to 300 × 300 nm^2.

lution standard made by Zhang et al. [27], and a dose of 30 nC/mm^2 was used in this experiment. In the exposure, every grid line is 10 pixels wide equivalent to 240 nm, and since the beam size is 300 nm FWHM then the exposed pattern should be around 540 nm. Next the sample was developed as described above using a second rinse step with fresh developer. Part of the resulting grid is shown in the SEM photo in Fig. 4, where it can be observed that the lines are about 800 nm wide. The sensitivity of the resist is 4 nC/mm^2, whereas a dose of 30 nC/mm^2 was used to guarantee the integrity of the structure: Previous tests have indicated that at lower doses the walls, particularly those with high aspect ratio, were not vertical, implying a less rigid structure. As can be observed, the higher dose increased the width of the lines compared to the design width.

3. Discussion

In this paper we have introduced two new resists for PBW. TiO_2 has great potential in optical applications. In the presented results the TiO_2 layer shows cracks after coating but for thinner layers this is not a problem [6], more research is necessary to optimize the coating procedure of thick layers. Because of the lower sensitivity of 8000 nC/mm^2 compared with PMMA and SU8 which have a sensitivity of 100 and 30 nC/mm^2 respectively, applications using this TiO_2 resist for PBW are rather time consuming; although improved brightness in a next generation proton beam writer will open more prospects for this resist.

WL-7154 has a lot of potential as a proton beam resist. We have shown it has high contrast ($\gamma = 6 \pm 1$) and high sensitivity (4 nC/mm^2), although this high sensitivity can give rise to unwanted resist hardening by scattered beam. Although sub-micron lines have been demonstrated, the development procedure has to be further optimized together with the administered proton dose to achieve even smaller structures in this resist.

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