Final Report AOARD 06-4004

Studies into sub 100 nm resists for Proton Beam Writing.

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I Aim of the project

Investigations into the characteristics of HSQ a new high resolution resists for p-beam writing, investigations into other potential resists for proton beam writing. Optimizing proton beam focusing through adjusted secondary electron detection. Develop computer models to simulate the interactions of the proton beam and resist below the 100 nm level to study proximity effects in proton beam writing.

II Scientific achievements

Our project AOARD 06-4004 has resulted in 5 scientific publications in the area of resist investigation for proton beam writing [1,2,3], optimized proton beam focusing through new methods of detecting secondary electrons [4] and theoretical calculations which show the absence of proximity effects in proton beam writing [5]. Main achievement: paper in nano letters in which HSQ is introduced as a superior resist for proton beam writing down to the 20 nm level [1].
In 2006-2007 we have also published 3 papers related to our AOARD 05-4037 project, one focused on the fabrication of microlenses [6] a second one on the optimized fabrication of resolution standards for proton beam writing [7]. A third paper discusses the use of proton beam writing for the fabrication of metal stencil masks for LIGA X-ray fabrication [8].
In 2006-2007 I have conducted 9 guest lectures and conference seminars on proton beam writing.

1. **Massachusetts Institute of Technology, Boston, USA, 2006.**
2. Charged Particle Optics Group, Faculty of Applied Sciences, Delft University of Technology, the Netherlands, 2007.
3. Physics department, Bristol University, UK, 2007.
4. CAFI-NEODE, Neuchatel, Switzerland, 2007.
5. Air Force Office of Scientific Research, Washington DC, USA, 2006, supported by the US air force through a WOS grant.
6. **Invited review talk: 2006** at the International Conference on Nuclear Microprobe Technology and applications / Second international Proton beam writing workshop (Singapore)
7. **Invited oral presentation** at NanoBiz Meet 2007, Singapore.
8. Oral presentation: 2007 7th High Aspect Ratio Microstructure Technology conference (Besancon, France).
9. Oral presentation: 2006 at the Materials Research Society Spring meeting, San Francisco.

In 2007 both Andrew Bettiol and Jeroen van Kan got promoted to assistant professor.

2007 OMICRON Prize for nano technology

In 2007 Jeroen van Kan has received the Omicron prize for his work on innovative nano technology research performed in Singapore. A large part of his work has been made possible through the support from the US air force under grant numbers: AOARD 04-4021, AOARD 05-4037 and AOARD 06-4004.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
05 JUL 2007	**FInal**	**31-05-2006 to 30-05-2007**

4. TITLE AND SUBTITLE
Studies into sub 100 nm resists for Proton Beam Writing.

5a. CONTRACT NUMBER
FA48690610031

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Jeroen van Kan

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Research Center for Nuclear Microscpy, Dept of Physics, National Univ ,of Singapore,Lower Kent Ridge Road,Singapore 119260,SP,119260

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO, AP, 96337-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-064004

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Our project AOARD 06-4004 has resulted in 5 scientific publications in the area of resist investigation for proton beam writing, optimized proton beam focusing through new methods of detecting secondary electrons and theoretical calculations which show the absence of proximity effects in proton beam writing. Main achievement: paper in nano letters in which HSQ is introduced as a superior resist for proton beam writing down to the 20 nm level. In 2006-2007 we have also published 3 papers related to our AOARD 05-4037 project, one focused on the fabrication of microlenses a second one on the optimized fabrication of resolution standards for proton beam writing. A third paper discusses the use of proton beam writing for the fabrication of metal stencil masks for LIGA X-ray fabrication.

15. SUBJECT TERMS
nanodevices, proton micromachining

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**6**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Resist investigations for proton beam writing

Three different resists have been investigated for their effectiveness in combination with PBW. Prior to the work described here the only compatible resists which have demonstrated sub-100 nm features are PMMA and SU-8. In this project, we have demonstrated that hydrogen silsesquioxane (HSQ) resist is a powerful non C based resist for PBW. The results obtained with PBW using the HSQ resist, show that HSQ behaves as a negative resist under proton beam exposure [1]. Details down to the 22 nm in width standing at a height of 850 nm have been directly written in HSQ see fig. 1. The superior resolution of HSQ shows great potential but unlike PMMA and SU-8 this resist has a limited shelf life. To optimize the usage of this resist contrast curves and sensitivity of HSQ as a function of shelf life have been measured [2], see fig. 2. We found that timing in HSQ resist processing is a critical factor in achieving nm sized features.

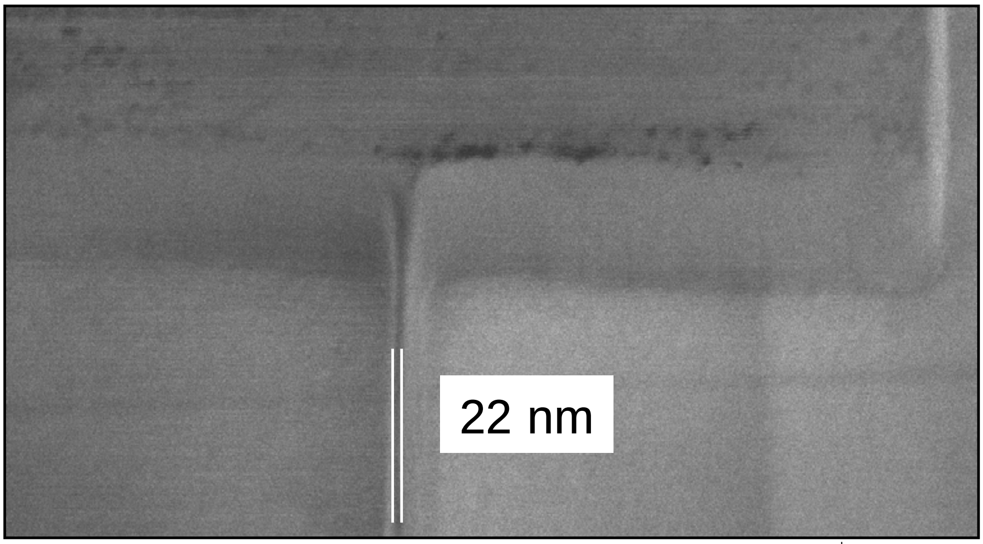

Fig 1 SEM images of a 22 nm wide line written with a 2 MeV $H2^+$ beam in 850 nm thick HSQ

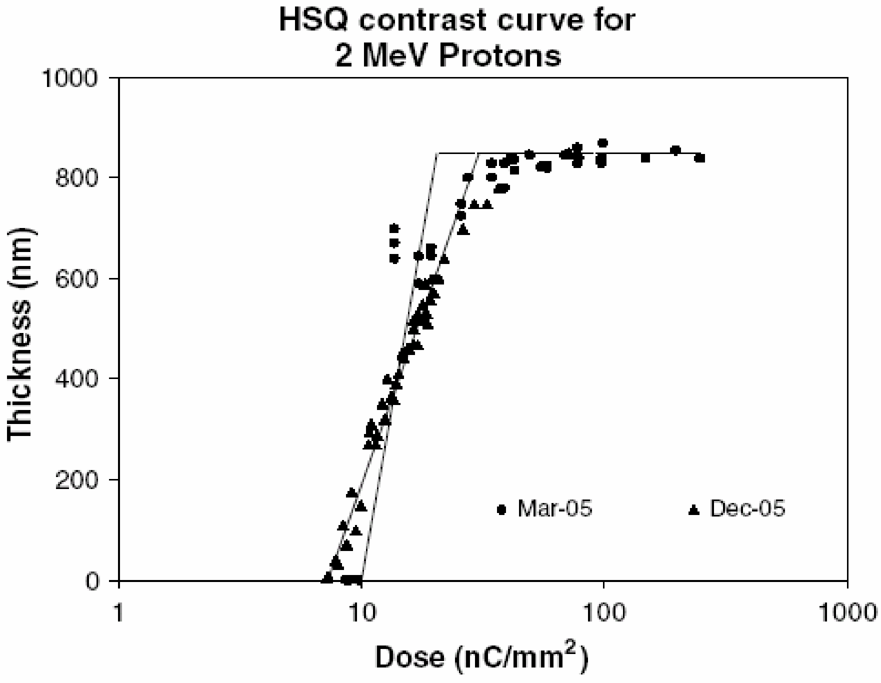

Fig 2 Contrast curve for 850 nm thick HSQ, exposed to 2MeV protons, the straight lines correspond to a contrast of 3.2 and 1.7 for the fresh and 10 month old resist, respectively.

The second 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, see fig. 3. Despite a relative low sensitivity of this resist for PBW (8000 nC/mm2) it has potential applications in the area of integrated optical components such as waveguides and gratings because of its high refractive index [3]. Further optimization is required to reduce the stress in the resist to avoid cracking of the resist during the drying of the resist after spincoating.

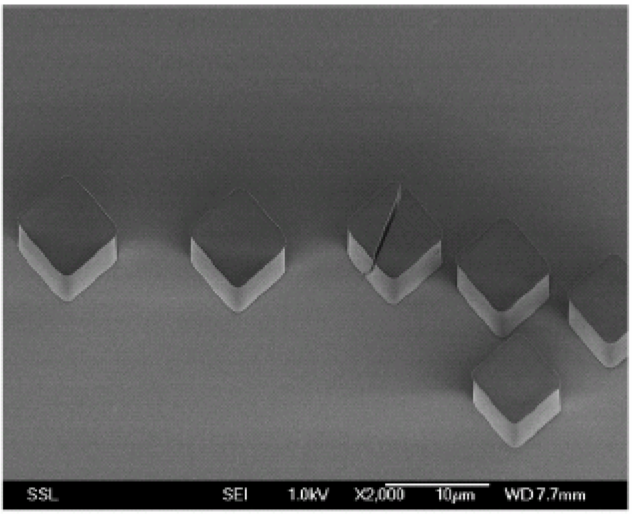

Fig. 3 SEM photo of 5x5 μm² squares in TiO, written with 1MeV protons applying a dose ranging from 10,000 up to 50,000 nC/mm2.

Finally WL-7154 a UV-sensitive negative resist has been evaluated in collaboration with Dow Corning. It shows high sensitivity for PBW (4 nC/mm^2). The first results show it is possible to write details below a micron in this resist, see fig 4. This resist could function as a mold for Ni electroplating to fabricate Ni stamps for nanoimprint- and soft-lithography [3].

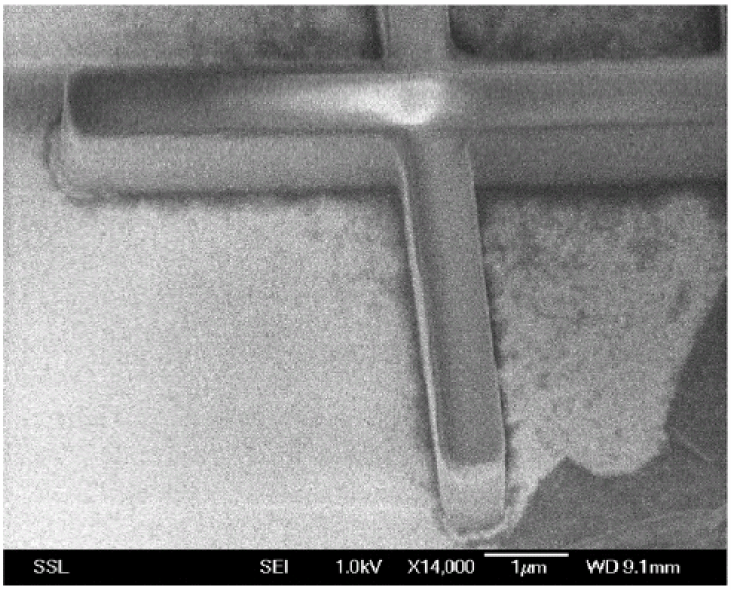

Fig. 4. SEM photo of sub-micron lines written in a 1.4 μm thick layer of WL-7154 using a 2 MeV proton beam focused down to 300×300 nm^2.

Optimized secondary electron imaging with protons

To make PBW more user-friendly it is important to have a fast way to focus the proton beam to small spot sizes. To quantity the focus of the proton beam a high resolution grid is imaged. The conventional mode of imaging used up to now has utilized conventional nuclear microprobe signals that are of a pulsed nature and are inherently slow. In this work, we report the new imaging system that has been introduced, which uses proton induced secondary electrons. This in conjunction with software developed in-house that uses a National Instruments DAQ card with hardware triggering, facilitates large data transfer rates enabling rapid imaging. Frame rates as much as 10 frames/s have been achieved at an imaging resolution of 512 x 512 pixels. The electron imaging system is based on attracting the electrons from the target. The system includes a cage and biasing ring, they are at positive potentials, attached to a glass tube. The cage first attracts the secondary electrons from the target which are then accelerated by the ring to impinge on a P-47 powder scintillator. The generated luminescence is then coupled via the quartz tube to a photomultiplier tube whose output current is amplified and converted into a voltage. Our imaging/scanning hardware uses these signals to generate fast high quality secondary electron images of our resolution standard. An example of a high resolution image of a Ni resolution standard is shown in fig. 5 (left) and compared with a conventional Rutherford backscatter image of the Ni grid (right) [4].

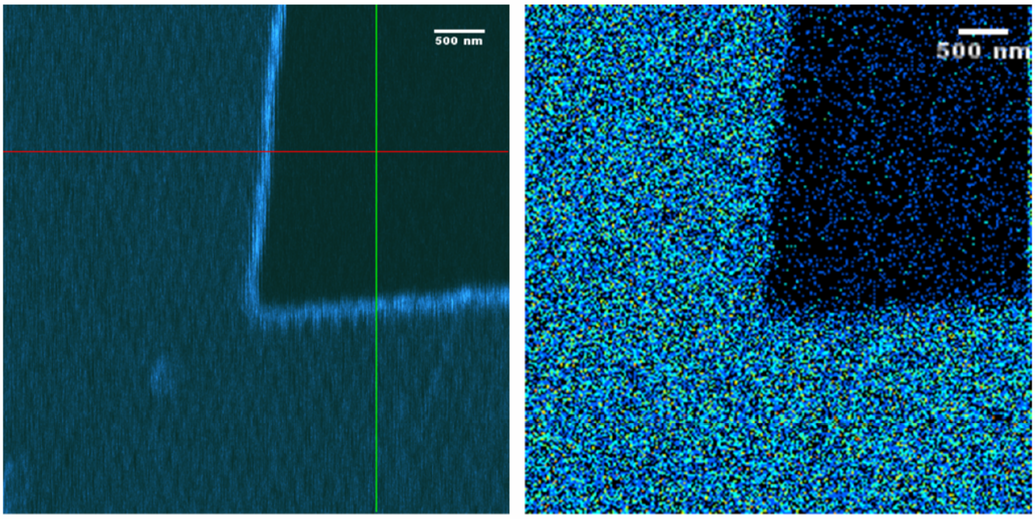

Fig. 5 Proton induced secondary electron image (left) and a conventional Rutherford back scatter image of a Ni grid resolution standard.

Calculations of proximity effects in proton beam writing

The generation of secondary electrons (or δ-rays) represents a significant mode of energy loss and energy delocalisation in the penetration of a charged particle into matter. Owing to the large mass disparity between electrons and protons, the trajectories of penetrating protons are essentially straight while those of electrons are tortuous and the fractional energy transferred to secondary electrons by individual protons are much less than with electrons. This suggests that protons are fundamentally capable of exhibiting superior proximity effects over electrons when used in lithography, no supporting evidence has yet been presented. In the present study we utilise the Hansen–Kocbach–Stolterfoht model for proton induced secondary electron emission to develop a Monte Carlo model capable of recreating the energy deposition profiles resulting from the creation and propagation of δ-rays produced by the passage of MeV protons in PMMA. In Fig 6 it is shown that after traveling 2 μm through a PMMA layer the energy deposited by a 2 MeV proton beam is well maintained within a radius of 10 nm whereas a 20 keV electron beam has completely spread over an area of more than 1 μm^2. We show that protons possess more confined energy deposition profiles than electrons. The simulation results presented in [5] are indicative of the superior nature of p-beam writing over e-beam writing with respect to the extent of proximity effects. The use of protons for lithography can result in more confined energy profiles while also permitting structures of high aspect ratios.

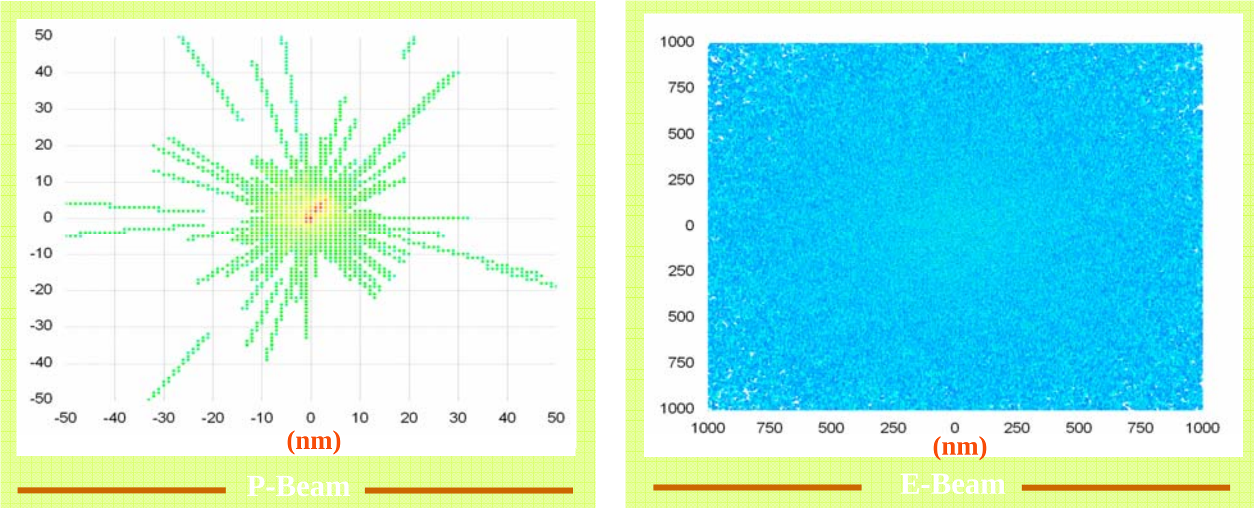

Fig 6 Energy deposition caused by generated δ-rays for a focused 2 MeV proton beam (left) and a focused 20 keV electron beam after traveling through 2 μm of PMMA resist.

Summary

We have introduced HSQ as new high resolution resist for proton beam writing. Structures down to the 20 nm level have been written in HSQ, standing at a height of 850nm. WL-7154 and TiO_2 resist have been evaluated. They don't have extreme resolution but could be used in areas like mold fabrication and specific optical applications respectively. A new fast electron detection system has been introduced which allows the fast and accurate focusing of MeV protons. Finally we have shown theoretically through Monte Carlo simulations that the proximity effects in proton beam writing are far superior compared with electron beam writing.

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