Available online at www.sciencedirect.com

ScienceDirect

Microelectronic Engineering 85 (2008) 945–948

MICROELECTRONIC ENGINEERING

www.elsevier.com/locate/mee

High aspect ratio micro/nano machining with proton beam writing on aqueous developable – easily stripped negative chemically-amplified resists

M. Chatzichristidi [a], E. Valamontes [b,e], P. Argitis [a], I. Raptis [a,*], J.A. van Kan [c,d], F. Zhang [d], F. Watt [d]

[a] Institute of Microelectronics, NCSR "Demokritos", Athens 15310, Greece
[b] Department of Electronics, Technological Institute of Athens, 12210 Aegaleo, Greece
[c] Engineering Science programme, Centre for Ion Beam Applications (CIBA), Physics Department, National University of Singapore, Singapore
[d] Centre for Ion Beam Applications (CIBA), Physics Department, National University of Singapore, Singapore
[e] Department of Telecommunications, University of Peloponnese, GR-22100 Tripoli, Greece

Received 7 October 2007; accepted 8 December 2007
Available online 8 January 2008

Abstract

Proton beam writing (PBW) is a new direct-writing process that uses a focused beam of MeV protons to pattern resist material at nano dimensions. PBW has the unique ability to maintain a straight path through 50 μm thick resist films, and is suitable for high aspect ratio micro(nano)-machining. TADEP resist is a new promising high aspect ratio chemically-amplified resist that can be developed in aqueous base developer and has the capability of stripping in conventional stripping schemes. By employing PBW on TADEP resist patterns with 280 nm linewidth and a thickness of 12 μm have been resolved showing an aspect ratio of 42. Following Ni electroplating of the TADEP features, Ni structures of height 0.8 μm and spacing of 167 nm, produced in 2 μm thick TADEP, were demonstrated indicating the easy stripping characteristics of the TADEP resist.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Micromachining; Nanomachining; Proton beam writing; Resist stripping; High aspect ratio

1. Introduction

The proton beam writing (PBW) which has been developed during the last years is a promising direct-writing methodology for the realization of high aspect ratio structures and critical lateral dimension in the micro- and nano-scale (HARM(N)), e.g. [1,2]. This writing technique, among other advantages that has over e-beam and focused ion beam fabrication, has the ability of penetrating thick resist films with the p-beam maintaining a straight path instead of the severe lateral scattering and backscattering encountered in the e-beam case. This exceptional capability makes PBW an ideal technique for the fabrication of high aspect ratio features in the nanometer scale region. In particular, PBW is the only direct-writing tool for fast prototyping of high aspect ratio structures with vertical walls up to 60 μm in height, for 2 MeV protons. Typical results demonstrated so far include the fabrication of a Ni stamp consisting of parallel ridges of 100 nm width, a 2 μm high structure fabricated in PMMA [3], high aspect ratio SU-8 wall structures of 60 nm width and 10 μm height [4], 22 nm wide lines written in 850 nm thick HSQ [5].

The resist materials implemented so far in this technology are also used for high resolution e-beam lithography, i.e. PMMA [6], HSQ [7], SU-8 [8]. The best high aspect ratio results have been obtained by SU-8. A typical problem however when using SU-8 for example as a template for pattern transfer to a metallic stamp using electroplating, is the inherent lack of stripping capability of SU-8.

* Corresponding author. Tel.: +30 210 650 3265; fax: +30 210 651 1723.
E-mail address: raptis@imel.demokritos.gr (I. Raptis).

0167-9317/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2007.12.005

Thus, the application of this particular material is limited only to applications where the SU-8 patterns play an active role rather a passive one. In previous works from NCSR 'Demokritos' the design and first patterning results of a novel negative aqueous base developable chemically amplified resist platform with better stripping characteristics compared to SU-8 have been presented [9,10].

In the present work the results of proton beam writing on an optimized version of that resist platform are presented along with very high resolution electroplating results.

2. Materials and patterning technology

In the present work, a specific formulation (Thick Aqueous Developable Epoxy resist, TADEP) of the aqueous base developable chemically-amplified resist platform with negative lithography behavior has been employed.

TADEP resist, is a new promising resist capable for resolving high aspect ratio structures that can be developed in aqueous base developer and has the ability of stripping in conventional stripping schemes. TADEP resist consists of partially hydrogenated poly(hydroxy styrene) (PHPHS), epoxy novolac (EP) and a sulfonium salt as the photoacid generator (PAG). The PHPHS has a hydrogenation of 8% and was purchased from Maruzen Co, the EP was obtained by fractionation of EPICOTE 164 from Shell and the PAG used was 1-(4-hydroxy-3-methylphenyl) tetrahydrothiophenium triflate (*o*-CS-triflate). The analogies of the components in the mixture are 80% w/w of PHPHS and 20% w/w of EP. The PAG content was 5% w/w with respect to the solids (polymer mixture) and the solvent use was ethyl(*S*)-(−)-lactate.

The p-beam writing was carried out at the CIBA-NUS using a dedicated p-beam writing set-up [12,13]. This system has the unique ability to focus p-beam down to sub 100 nm spot sizes. P-beam writing of the TADEP resist was performed using 2 MeV protons. The exposure field used in these experiments was $40 \times 40\ \mu m^2$ with a beam step size of 10 nm. The beam size was 100×200 nm for the first film thickness and 200×250 nm for the second.

For the pattern transfer to a metal film a nickel electroplating process was utilised. For the electroplating experiments, the Si wafer was pre-coated with a seed layer of Cr (10 nm)/Au (100 nm) and a single step nickel sulfamate plating process was used. The stripping of the 2 μm resist was achieved by immersion of the sample in acetone for 5 min and subsequent use of ultrasonic bath for 10 min.

3. Results

3.1. PBW simulation

In order to reveal the potential of PBW for high aspect ratio patterning with very limited lateral broadening, a complete model of proton energy transfer from proton beam, to matter was developed and applied. To build a complete model of proton energy loss in lithographies, two issues have to be addressed: The first is the proton scattering process in the materials (propagation) and the second is how the energy is transferred from protons to the photoresist (deposition). To understand the proton scattering process, the continuous slowing down approximation (CSDA) has been used in our Monte Carlo simulations. The propagation of a proton can be well described by the CSDA, but this model does not give any information on local chemical processes. Finally, the protons travel in free flight between elastic interactions.

The formalism adopted for simulating protons propagation is that of TRIM/STRIM [14,15]. The electronic stopping powers at high energies were calculated according to Bethe's theory with various refinements (shell corrections, corrections for departures from the first Born approximation and the density effect correction). At low energies, electronic stopping powers were obtained from experimental data, with heavy reliance on empirical fitting formulas developed by Andersen and Ziegler [16]. Nuclear stopping powers were obtained by calculating the transfer of energy to the recoiling atoms in elastic collisions. The cross section for the elastic scattering by atoms was obtained by a classical trajectory calculation according to the method of Everhart et al. [16]. Finally, mean excitation energies for compounds were obtained by using Bragg's additivity rule.

In Fig. 1 the energy deposited at the interface of 10 μm thick resist film over bulk Si substrate vs. the lateral distance is illustrated where it is clear that the broadening is very small.

3.2. Resist formulation and patterning mechanism

For the evaluation of the lithographic performance of the TADEP resist in PBW two resist formulations were prepared. A 45% w/w solution in ethyl-*s*-lactate gave film thickness from 10 to 55 μm and a 30% w/w solution gave film thickness from 2 to 10 μm. Typical film thickness vs. spin coating speed results are presented in Fig. 2.

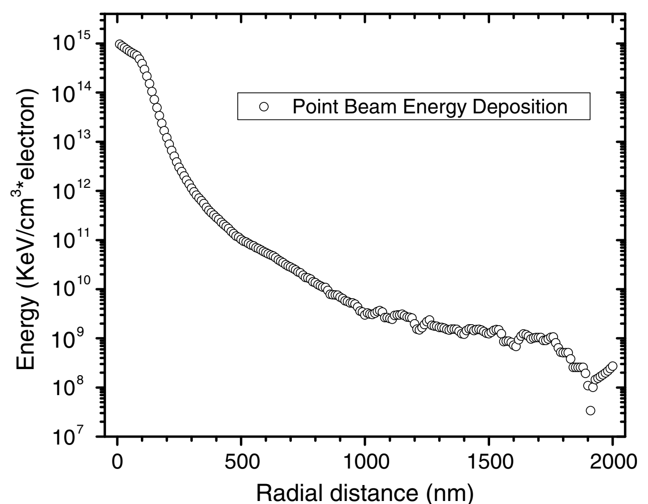

Fig. 1. Energy deposition at the interface of a 10 μm resist film over Si substrate.

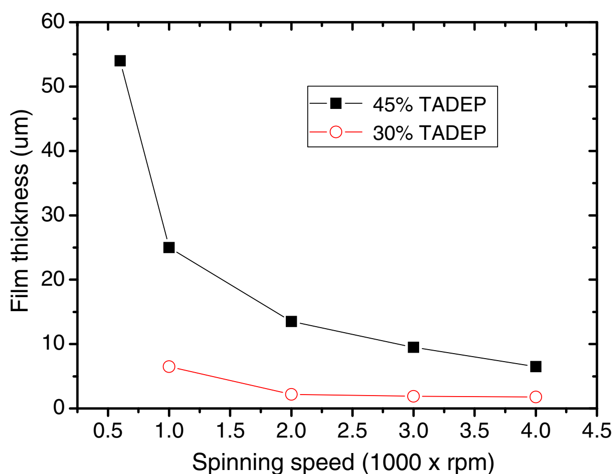

Fig. 2. Film thickness vs. spinning speed for resist formulations with 30% and 45% w/w polymer and 5% PAG concentrations in ethyl lactate.

Two TADEP resist film thicknesses were investigated in the present work: 2 and 12 μm. In order to achieve a 2 μm film the 30% w/w resist formulation was spin coated on a Si wafer at 3500 rpm for 30 s. Both thermal processing steps post applied bake (PAB) and post exposure bake (PEB) were carried out on a leveled hot plate. The PAB step was performed at 95 °C for 1 h. The film was exposed by the proton beam followed by PEB at 110 °C for 2 min. Development was made using TMAH 0.26 N (AZ-726MIF from AZ-EM) for 2 min. The 12 μm film thickness was achieved by spin coating the 45% w/w resist formulation at 3000 rpm for 30 s. PAB was performed at 95 °C for 2 h, PEB at 110 °C for 8 min and development time, in stirring mode, was 8 min. It should be noted that the samples, covered with the TADEP films after spin coating and PAB, were shipped to NUS for further processing (exposure, PEB, development) and show a very good stability and process latitude in terms of film quality and shelf life.

Upon exposure, protons are generated from the PAG and during PEB these protons open the epoxy rings of EP that are subsequently attached to the hydroxyl groups of the PHPHS to create a crosslink network. The crosslink network is less dense than that of SU-8 (comprising an epoxy with eight epoxy rings in its molecule as the basic component) as it is "diluted" from the PHPHS polymer which is now the main component of the formulation. It is more probable that an opened epoxy ring will bond to a hydroxyl than to another epoxy ring due to the fact that the resist contains 80% of PHPHS and the polymer mixture is fully miscible [11]. The proposed chemistry is showed in Fig. 3.

In Fig. 4 SEM images from the high resolution patterns in the 12 μm thick TADEP films after development are illustrated. In this case the layout line consists of 2-pixel wide lines. In Fig. 4a a top-view SEM image is shown where the measured linewidth was observed to be 280 nm in the x-direction and 330 nm in the y-direction. These values are very close to the beam diameter used, ~200 × 250 nm showing the excellent properties of the TADEP resist and PBW in

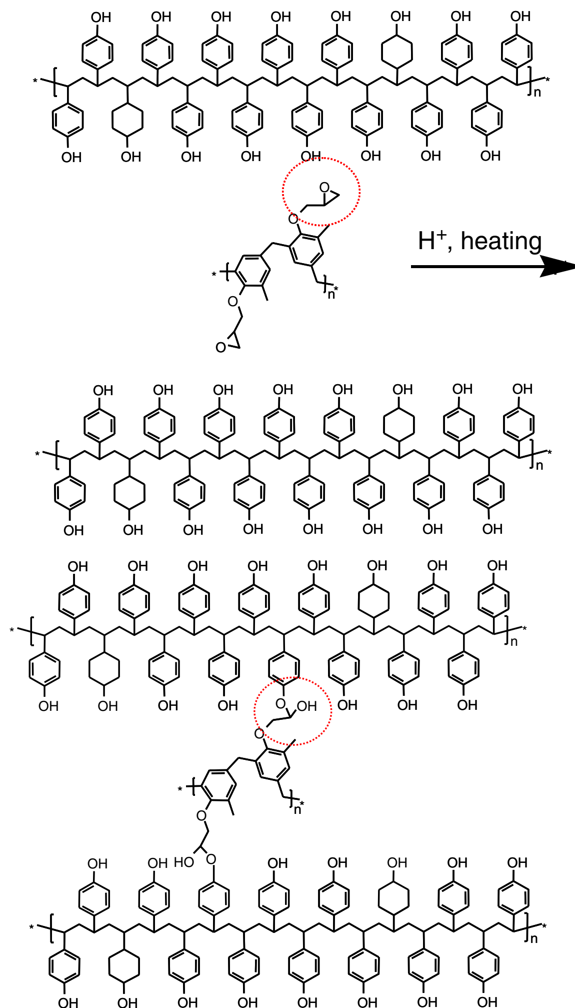

Fig. 3. Schematic presentation of the crosslinking mechanism of the TADEP resist.

terms of acid diffusion and almost vertical penetration of the protons. The fabricated grid structure has a 4 μm pitch size, and the aspect ratio achieved is 42 (Fig. 4b). It is noticeable that using aqueous base development the film was fully developed without any collapse of the lines. This result was accomplished after optimization of the resist. The PAG and the lower degree of hydrogenation specific PHPHS used, made the new resist more hydrophilic than formulations previous reported [8–11] and hence the development was better controlled and with higher development rate. The resist walls are observed to be very smooth and vertical due to the parallel beam path of proton beam and the even energy deposition of the proton beam along its path. The line edges are very smooth due to the stability of the proton beam writing system.

The aspect ratio achieved is not as high as in the SU-8 (~160) and possibly could be improved by the use for a beam with smaller diameter.

The 2 μm TADEP film was exposed using proton beam writing, and the developed pattern is shown in Fig. 5a. The patterned wafer, which had been pre-coated with a seed layer of Cr (10 nm)/Au (100 nm), was then electroplated

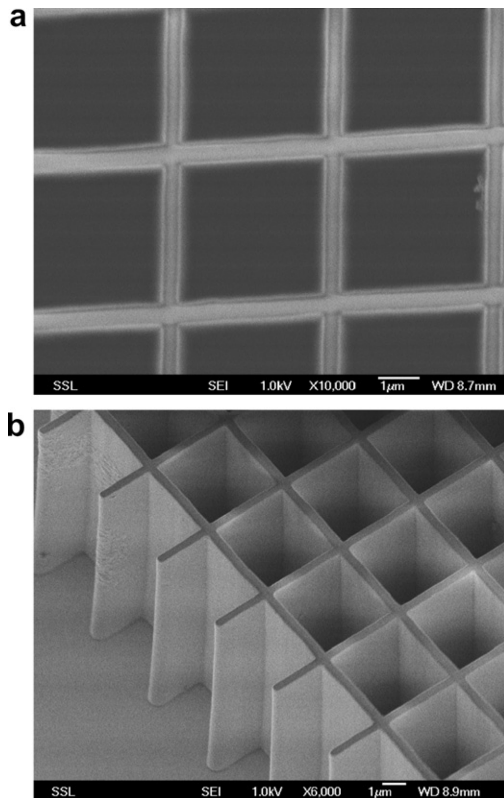

Fig. 4. SEM images of PBW double line irradiation on TADEP resist. Film thickness 12 μm, line width 280 nm in x-direction, aspect ratio: 42. (a) Top view and (b) side view (tilt 20°).

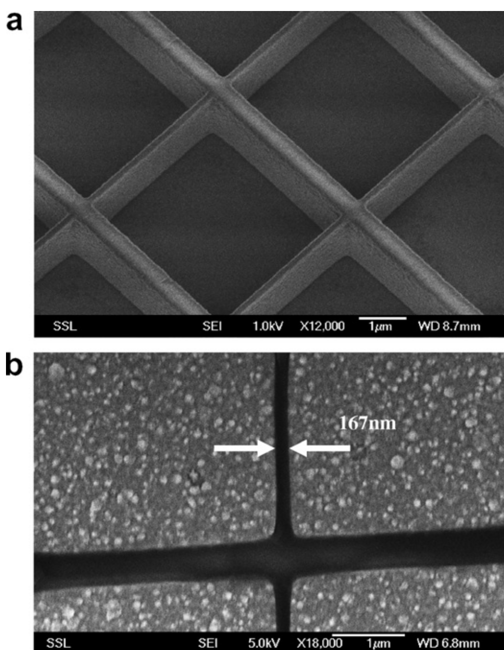

Fig. 5. SEM images of PBW double line irradiation on TADEP resist. (a) Film thickness 2 μm, line width 167 nm in x-direction, pitch size 4 μm. (b) Electroplating and strip-off of the above pattern. The nickel structures have a thickness of 0.8 μm.

in a nickel sulfamate bath giving Ni structures of 0.8 μm thickness (see Fig. 5b). The distance between the metal features is 167 nm, virtually the same size as the width of the resist wall in the x-direction (Fig. 5a). The successful electroplating process provides strong evidence of complete resist development as well as a successful strip-off process.

4. Conclusions

Proton beam writing technology, due to its unique ability to maintain a straight path through 60 μm thick resist films, is suitable for high aspect ratio micro(nano)-machining. TADEP resist is a new promising high aspect ratio chemically amplified resist that can be developed in aqueous base developer and has the capability of stripping in conventional stripping schemes. By employing PBW on TADEP resist a 280 nm linewidth with a thickness of 12 μm has been resolved showing an aspect ratio of 42. In addition, Ni features of 0.8 μm and spacing of 167 nm were demonstrated proving the easy stripping of the TADEP resist.

Acknowledgments

We thank the Greek Secretariat for Research & Technology contract number 05-NONEU-467, PB.NANO-COMP project, for funding this work. Authors would like to thank Dr. Th. Speliotis for the preparation of the wafers for the electroplating.

References

[1] F. Watt, M.B.H. Breese, A.A. Bettiol, J.A. van Kan, Materials Today 10 (6) (2007) 20.
[2] K. Ansari, J.A. van Kan, A.A. Bettiol, F. Watt, Appl. Phys. Lett. 85 (2004) 476.
[3] K. Ansari, J.A. van Kan, A.A. Bettiol, F. Watt, J. Micromech. Microeng. 16 (2006) 1967.
[4] J.A. van Kan, P.G. Shao, K. Ansari, A.A. Betiol, T. Osipowicz, F. Watt, Microsyst. Technol. 13 (2007) 431.
[5] J.A. van Kan, A.A. Bettiol, F. Watt, Nano Lett. 6 (2006) 579.
[6] N. Uchiya, T. Harada, M. Murai, H. Nishikawa, J. Haga, T. Sato, Y. Ishii, T. Kamiya, Nucl. Instrum. Meth. B 260 (2007) 405.
[7] J.A. van Kan, A.A. Bettiol, F. Watt, Nucl. Instrum. Meth. B 260 (2007) 396.
[8] I. Rajta, M. Chatzichristidi, E. Baradács, C. Cserháti, I. Raptis, K. Manol, E.S. Valamontes, Nucl. Instrum. Meth. B 260 (2007) 414.
[9] M. Chatzichristidi, I. Raptis, C.D. Diakoumakos, N. Glezos, P. Argitis, Microelectron. Eng. 61 (2002) 729.
[10] I. Rajta, E. Baradacs, M. Chatzichristidi, E.S. Valamontes, I. Uzonyi, I. Raptis, Nucl. Instrum. Meth. B 231 (2005) 423.
[11] M. Chatzichristidi, I. Raptis, P. Argitis, J. Everett, J. Vac. Sci. Technol. B 20 (2002) 2968.
[12] C.N.B. Udalagama, A.A. Bettiol, J.A. van Kan, F. Watt, Nucl. Instrum. Meth. B 210 (2003) 256.
[13] J.A. van Kan, A.A. Bettiol, F. Watt, Appl. Phys. Lett. 83 (2003) 1629.
[14] J. Biersack, L. Haggmark, Nucl. Instrum. Meth. 174 (1980) 257.
[15] J.F. Ziegler, J.P. Biersack, U. Littmark, The stopping and range of ions in solids, The Stopping and Ranges of Ions in Matter, vol. 1, Pergamon Press Inc., 1985.
[16] Stopping Powers and Ranges For Protons And Alpha Particles, International Commission on Radiation Units and Measurements, Report 49, 1993.