Step and repeat UV nanoimprint lithography on pre-spin coated resist film: a promising route for fabricating nanodevices

2010 Nanotechnology 21 445301

(http://iopscience.iop.org/0957-4484/21/44/445301)

IOP PUBLISHING NANOTECHNOLOGY

Nanotechnology **21** (2010) 445301 (5pp) doi:10.1088/0957-4484/21/44/445301

Step and repeat UV nanoimprint lithography on pre-spin coated resist film: a promising route for fabricating nanodevices

C Peroz[1], S Dhuey[2], M Volger[3], Y Wu[4], D Olynick[2] and S Cabrini[2]

[1] aBeam Technologies, 5286 Dunnigan Court, Castro Valley, CA 94546, USA
[2] The Molecular Foundry, LBNL, One Cyclotron Road, Berkeley, CA 94702, USA
[3] MicroResist Technology, Köpenicker Straße 325, 12555 Berlin, Germany
[4] Oxford Instruments, 300 Baker Avenue, Suite 150, Concord, MA 01742, USA

E-mail: cp@abeamtech.com

Received 4 August 2010, in final form 15 September 2010
Published 5 October 2010
Online at stacks.iop.org/Nano/21/445301

Abstract

A step and repeat UV nanoimprint lithography process on pre-spin coated resist film is demonstrated for patterning a large area with features sizes down to sub-15 nm. The high fidelity between the template and imprinted structures is verified with a difference in their line edge roughness of less than 0.5 nm (3σ deviation value). The imprinted pattern's residual layer is well controlled to allow direct pattern transfer from the resist into functional materials with very high resolution. The process is suitable for fabricating numerous nanodevices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanoimprint lithography (NIL) is a powerful approach for patterning surfaces at the nanometer scale over large areas at low cost and high throughput. Numerous applications from nanophotonics to nanofluidics will benefit from this technique for scaling down actual devices and/or developing new devices. NIL basically consists of stamping deformable surfaces with a nanostructured template. There are two main versions of the NIL method depending on the nature of the imprinting materials: thermal-NIL, which uses the thermo-mechanical properties of films [1, 2], and UV-NIL, in which a liquid resist material is cured by ultraviolet light [3, 4]. Over the last 10 years, the UV-NIL approach has gained several important advantages in term of throughput and overlay [5, 6] and is in the pre-production phase for various 'conventional applications' such as hard disks and liquid crystal displays.

Key issues limiting the emergence of UV-NIL for several applications are mainly the fabrication of high quality templates with high-resolution features, the control of the residual layer thickness underneath the imprinted structures and defect counts related to the imprint process. The most popular solution is to dispense droplets of very low viscosity resist (typically $\eta < 5$ m Pa s) in a predetermined die and to imprint the resist at low pressure and at room temperature. The method was developed first by Willson's group [7] and is commonly called 'step and flash imprint lithography' (S-FIL). In this technique, an array of droplets of photopolymerizable organosilicon resist are imprinted with a small quartz mold by capillary action. By analogy with an optical lithography stepper, successive imprints can be repeated in order to pattern a large area: this is the step and repeat imprint (SR-NIL) process. The SR-NIL approach also allows us to simplify the fabrication of templates by limiting their sizes and thus reducing their cost.

For example, a SR-NIL tool developed by Molecular Imprints has demonstrated resist patterning of isolated lines down to 11 nm over an 8 inch wafer, but the pattern transfer from resist to another material is limited to 28 nm half-pitch gratings at the time of writing [8]. The gap between the minimum feature sizes which can be imprinted and which can be really transferred into functional materials is governed by the residual layer underneath the imprinted pattern. As a general rule, the thinner and more uniform the residual

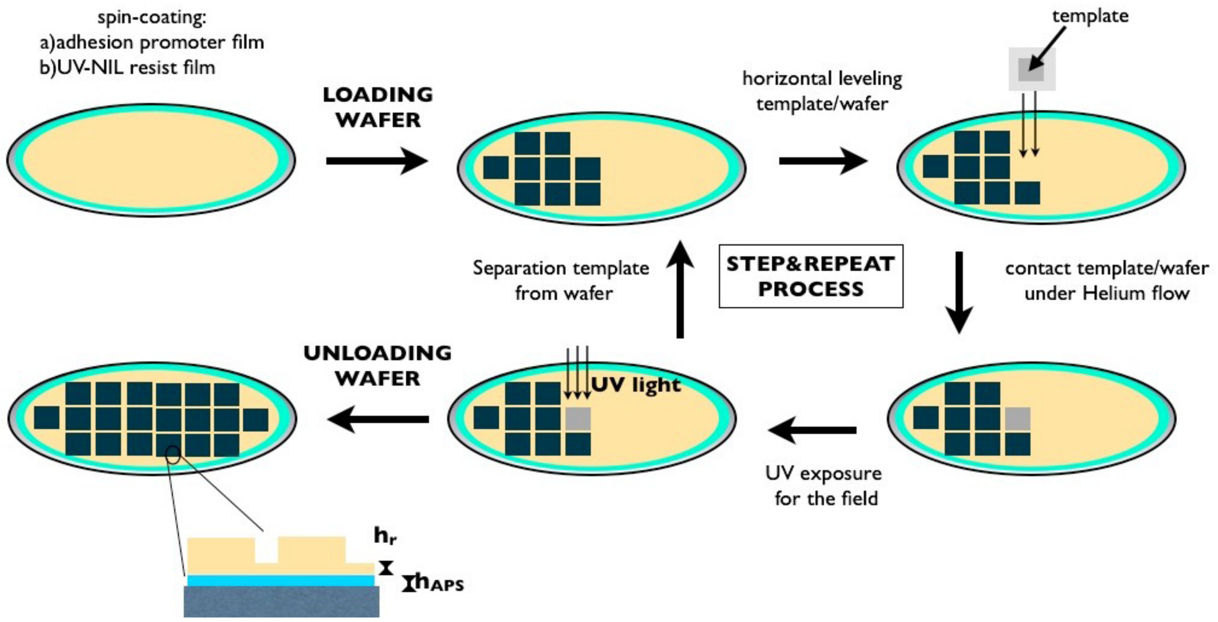

Figure 1. Process flow for step and repeat UV NIL on pre-spin coated resist films.

layer thickness (RLT), the better the pattern transfer. For the S-FIL process, the main efforts are currently aimed at decreasing the initial volume of dispensed droplets and optimizing the dispensing method in order to achieve a thinner and more uniform residual layer thickness. Numerical models taking account of the physico-chemical properties of the resist (viscosity, evaporation rate) and the pattern geometry of the mold aid in developing the appropriate droplet-dispensing recipe [9]. The best values for RLT achieved by S-FIL are around 12 nm [7–9].

Based on the conviction that there is not one superior NIL solution but that conversely we need to develop one specific process to imprint particular materials depending on the intended application and its requirements, we introduce in the present paper an alternative NIL process. Our strategy consists of combining advantages of both step and repeat technology and imprinting on pre-spin coated resist films [6, 10, 11] to pattern a large area with feature sizes down to sub-15 nm. The residual layer thickness and its uniformity are easily controlled and allow the smallest patterns reported into the literature to be transferred into functional materials [12]. The method is scalable to large areas and is suitable for fabricating nanodevices at high throughput and low cost.

2. Experimental details

Figure 1 describes the SR-NIL process on pre-spin coated films. First, a sub-5 nm film of aminoalkyl–trimethoxysilane solution (mr-APS1 from Microresist Technology [13]) is spin coated and baked on 6 inch wafers to promote the adhesion of the UV-NIL resist. The trimethoxysilane part of the adhesion promoter film leads reactive molecules to form covalent bonds to the Si or SiO_2 substrate surfaces, whereas the aminoalkyl groups of APS promote adhesion of the NIL resist. A UV-NIL resist (mrUV-Cur21 from Microresist Technology [14]) is then spin coated and soft baked to create uniform solvent-free resist films. In contrast to common materials used for SR-NIL, this resist is a purely organic (silicon-free) material composed of multifunctional acrylate monomers and a mixture of photo-initiators. The specific chemistry of the resist prevent it from cross-linking in the presence of oxygen, limiting its UV curing to the imprinted area where the NIL mold is in contact with the resist. The thickness is varied here between 60 and 120 nm depending on the concentration of the resist within the spin solvent and the spin conditions. Spin speed is typically tuned between 1000 and 5000 rpm for 45 s. After the post-applied bake at 80 °C for 1 min, the remaining liquid polymer has a dynamic viscosity around 30 m Pa s [14], low enough to fill nano-cavities of the template by capillary action. The imprint step is carried out with an Imprio 55 press from Molecular Imprints Inc. Before imprinting, the template is treated with an anti-sticking layer in two steps: (1) the surface of the mold is activated by an oxygen plasma at low power and (2) a self-assembled layer of 1H,1H,2H,2H-perfluoro-octyltriethoxysilane is deposited by vapor evaporation [14].

During the imprint process, the quartz template is horizontally leveled with the substrate/resist system and pressed onto the film at room temperature and at low pressure (force < 30 N). A helium gas flow is applied during the template contact phase to avoid the trapping of air bubbles between the template and the resist [15] and to promote the cross-linking of the resist by displacement of the air in the vicinity of the imprinted area. While the template is in contact with the substrate, the resist is cured by UV light and the mold is released from the substrate. This process is repeated on each die of the wafer. The total time for one imprint operation is less than 2 min per die.

The quality of the final imprint depends implicitly on the quality of the template. We have produced templates in a single lithographic step without the need for pattern transfer [16]. Our

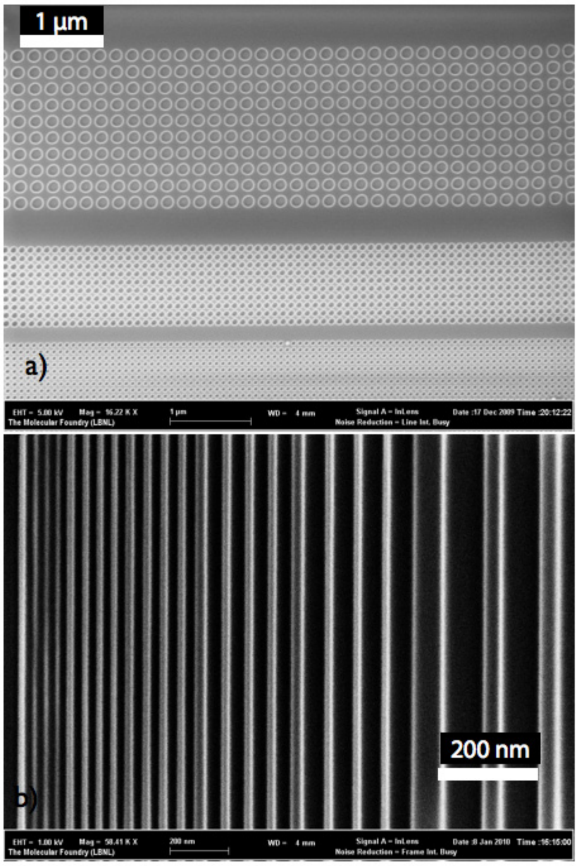

Figure 2. Scanning electron microscope pictures of imprinted structures. (a) Array of holes with variable diameters/pitch sizes: 100/200, 60/100, 40/80 nm from top to bottom. (b) Gratings with variable linewidth/pitch: 13/30, 20/50, 25/60, 30/80, 35/100, 60/200.

imprint templates consist of a 65 mm square substrate, with a centered 25 mm square mesa which is raised 15 μm above the surrounding field. The 25 mm mesa contains hydrogen silsesquioxane (HSQ) nanostructures and is the only part in contact with resist during the imprinting process. HSQ resist is directly patterned on the template surface, the 'mesa quartz template', using electron beam lithography (EBL). This allows templates to be fabricated without etching, which can be problematic for small features. The EBL process is performed at an accelerating voltage of 100 kV and a beam current of 500 pA. A commercial negative HSQ resist diluted at 2–6% volume in methyl isobutyl ketone is spin coated to reach film thicknesses between 50 and 120 nm. In addition, a 60 nm thick layer of conductive polymer (Aquasave from Mitsubishi Rayon) is spin coated on the top of the HSQ films in order to minimize charging effects associated with the insulating quartz wafer. Exposure doses for EBL vary between 3 and 40 mC cm^{-2} according to the feature sizes and density of the patterns. Salty development in an aqueous mixture of 1 wt% NaOH and 4% wt NaCl for 4 min is used to reach high contrast and resolution down to 10 nm [17].

3. Results and discussion

Examples of various imprinted patterns are depicted in figure 2. Gratings with variable pitch between 2 μm and 40 nm as well as arrays of holes with a diameter between 40 and 100 nm have been successfully imprinted from the same mold. The dies are replicated with our SR-NIL process over 6 inch wafers. Features down to 13 nm are imprinted. The resolution limit is unknown at the time of writing but seems essentially limited by the template. Pattern fidelity between the mold and the imprinted features is investigated using three metrics: critical dimension (CD), line edge roughness (LER) and line width roughness (LWR). myCD software is used to accurately extract CDs, LWR (3σ) and LER (3σ) values out of top-view scanning electron microscope images. The software uses a physical model of SEM and was recently verified by the industry (see [18, 19]). Figure 3 shows the metrological parameters for high-resolution gratings. The extracted contours for trenches of the gratings in the HSQ mold are compared to contours of imprinted lines in the UV-NIL resist (see table 1). The dimensional stability of our imprint process is demonstrated with mold/imprint CD changes smaller than 4 nm and LER and LWR changes below 0.5 nm. The minor differences between linewidth values for trenches M1, M2 and M3 are inside the range of LWR uncertainty. We believe that this difference is due to the lithographic process for fabricating the mold and shows the ultimate resolution limit of our process.

Table 1. CD, LWR and LER values and the deviations between the mold and imprinted features ΔCD, ΔLWR, ΔLER. CD values are determined at 50% of pattern height and LWR and LER are 3σ deviation values. Values for imprinted lines were measured at two different locations around 50 μm apart.

	m1	i1	m2	I2	m3	i3
50% CD (nm)	16.9	13.9	16.6	13.1	15.9	13.4
LWR (nm)	1.5	2.0	1.6	2.0	1.7	2.0
LER (nm)	1.4	1.9	1.4	1.8	1.3	1.9
Δ50% CD (nm)	3		3.5		2.5	
ΔLWR (nm)	0.5		0.4		0.3	
ΔLER (nm)	0.5		0.4		0.6	

a residual layer of resist underneath the imprinted patterns is one of the key issues for transferring imprinted structures from the resist to other functional materials and fabricating real devices. As defined in figure 1, the residual layer thickness (RLT) is the sum of the residual layer thickness of the imprint resist (h_r) and the thickness of the adhesion layer (h_{APS}): RLT $= h_r + h_{APS}$. We found that the values of h_r and h_{APS} are easily tuned by changing the spin coating conditions and the concentration of the resist solution. Figure 4 shows RLT values for two imprints performed with the same mold (feature height ≈ 100 nm) and adhesion layer thickness ($h_{APS} \approx 3$ nm). The initial thickness of the resist film is fixed to 120 nm (figure 4(a)) and 100 nm (figure 4(b)). The corresponding RLT values are 13.5 and 3.5 nm, whereas the residual layer thickness due to the resist alone (h_r) is approximately 10 nm for a 120 nm thick initial film and is quasi-zero for the thinner resist film. Thus, we can carefully control the RLT values and reach sub-5 nm thick residual layers (h_r) by simply tuning the initial resist thickness. A minimum residual layer thickness is needed to avoid the problem of adhesion of the resist on the substrate and prevent the appearance of defects during demolding. SEM cross-sections have been measured at five random places over

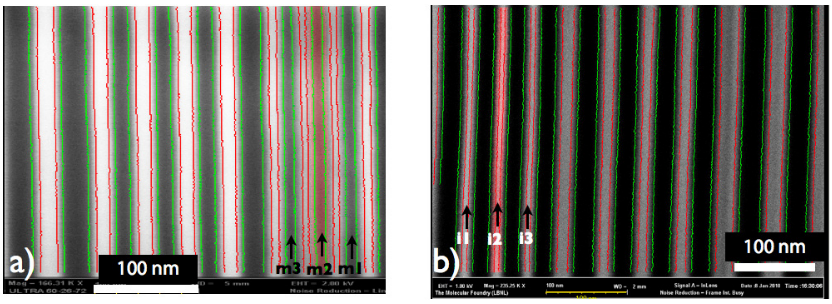

Figure 3. SEM images of 50 nm thick HSQ gratings on silicon and its replication into 50 nm thick UV-NIL resist. Automatic extraction of contours using myCD software are displayed at the top and bottom of patterns: (a) the trenches in the template and (b) the corresponding imprinted lines.

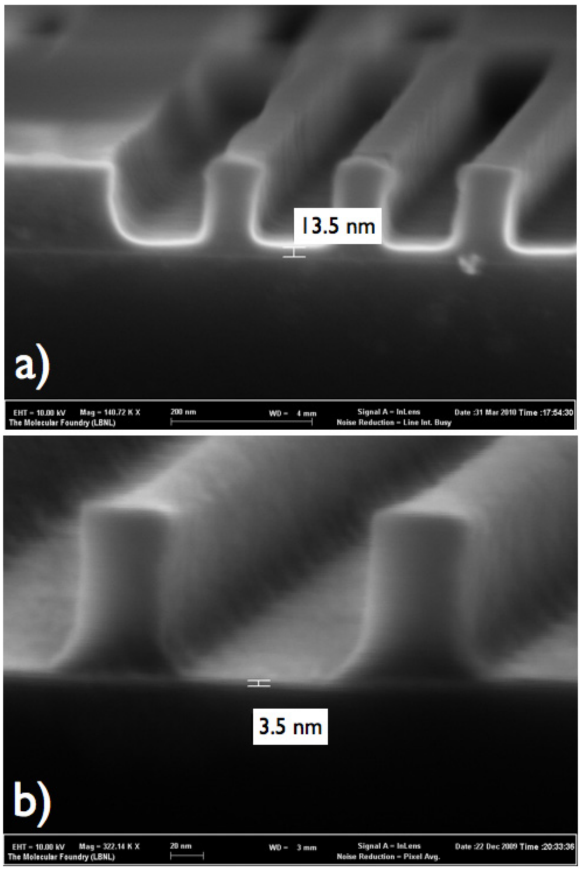

Figure 4. SEM cross-section images of two identical imprinted gratings for initial an thickness of the resist film of (a) 120 nm (b) 100 nm. The height of features in the mold is around 100 nm.

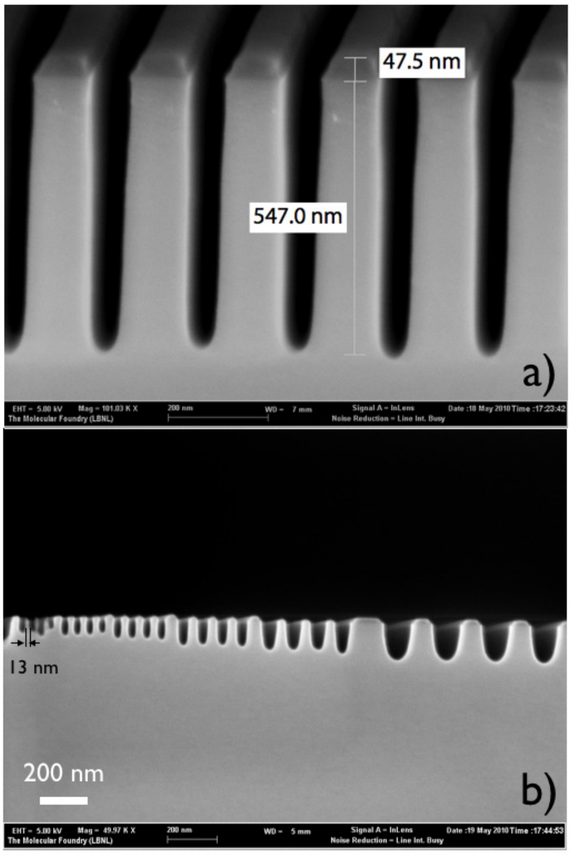

Figure 5. SEM pictures of imprinted gratings after transfer into silicon wafers. (a) 90 nm linewidth gratings with 547 nm depth into silicon and 47.5 nm thick UV-NIL resist remaining after the etching steps. (b) Grating with variable pitch/linewidth corresponding to figure 2(b). The minimum feature size is 13 nm with an etching depth of around 50 nm.

each grating, with variable pitches, of several tens of square millimeters imprinted at six different dies. The RLT uniformity is approximately 3 nm for $h_r \approx 13$ nm. The importance of the achieved uniform and thin RLT cannot be underestimated for pattern transfer at the nanometer scale. During nanoscale etching, the shape of the mask is very important for getting high fidelity pattern transfer. Deviations from the ideal mask shape translate to poorly transferred patterns. The act of descumming the residual layer can round-off the imprinted resist features and result in deviations in CD [20]. Examples of patterns transferred into silicon are shown in figure 5. The residual layer is etched first by reactive ion etching (RIE) with a gas mixture of CHF_3 and O_2. Then the imprinted patterns are transferred into silicon at cryogenic temperatures with SF_6 and O_2 gases in an Oxford Plasmalab 100 with a Cobra ICP source. Figure 5(a) demonstrates that the etching selectivity between the imprint resist and the silicon is higher than 1:15 allowing high process latitude. As an example, nanostructures with an aspect ratio greater than six are depicted in figure 5(a). Our process eased the transfer of imprinted pattern from the resist into functional materials with a fine control of the thickness and of the uniformity of the residual layer. Maintaining the fidelity of the resist mask by controlling the RLT allows us to transfer features down to 13 nm as shown in figure 5(b). The variation of the height as a function of feature size is due to RIE lag and is not an artifact of the imprint process. Details of the development of the SF_6/O_2 cryogenic etching process for nanoscale features will be presented in a separate work.

4. Conclusion

We have demonstrated a promising nanoimprinting process which combines the advantages of step and repeat NIL and imprinting of spin-on resist. The simplified template fabrication process is completed with a single exposure step and allows high-resolution patterning. The imprinting step is performed at ambient temperature and low pressure with a resolution down to 13 nm. The residual layer thickness can be reduced to sub-5 nm thickness and is uniform over large areas. This fine control of the residual layer is crucial for high-resolution pattern transfer. To our knowledge, this is the highest resolution imprinted feature to be directly pattern transferred via plasma etching. The selectivity of the etching process to the imprint resist allows transfer into silicon of features with a high aspect ratio. We strongly believe that this method offers an alternative way to fabricate photonics or other nanofluidic chips at low cost and high throughput.

Acknowledgments

We would like to thank B Harteneck and E Wood for their technical support and S Babin for providing myCD software analysis. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under contract no. DE-AC02-05CH11231.

References

[1] Chou S Y, Krauss P R and Renstrom P J 1996 *Science* **272** 85
[2] Peroz C, Chauveau V, Barthel E and Sondergard E 2009 *Adv. Mater.* **21** 555
[3] Haisma J, Verheijen M, Heuvel K v D and Berg J v D 1996 *J. Vac. Sci. Technol.* B **14** 4124
[4] Austin M D, Ge H, Wu W, Li M, Yu Z, Wasserman D, Lyon S A and Chou S Y 2004 *Appl. Phys. Lett.* **84** 5299
[5] Stewart M D, Johnson S C and Sreenivasan S V 2005 *J. Microlith. Microfab. Microsyst.* **4** 011002
[6] Bender M, Fuchs A, Plachetka U and Kurz H 2006 *Microelectron. Eng.* **83** 827–30
[7] Michaelson T, Sreenivasan S V, Ekerdt J and Willson C G 1999 *Proc. SPIE* **3676** 379–89
[8] Resnick D 2010 *EIPBN Conf. (Anchorage, AK)*
[9] Kim K D, Jeong J H, Sim Y S and Lee E S 2006 *Microelectron. Eng.* **83** 847–50
[10] Otto M, Bender M, Richter F, Hadam B, Kliem T, Jede R, Spangenberg B and Kurz H 2004 *Microelectron. Eng.* **73** 152
[11] Otto M, Bender M, Zhang J, Fuchs A, Wahlbrink T, Bolten J, Spangenberg B and Kurz H 2007 *Microelectron. Eng.* **84** 980
[12] Morecroft D, Yang J K W, Schuster S, Berggren K K, Xia Q, Wu W and Williams R S 2009 *J. Vac. Sci. Technol.* B **27** 2837
[13] Adhesion promoter mr-APS1 and UV–NIL resist mr-UVCur21 commercially available from micro resist technology GmbH, Germany www.microresist.com
[14] Beck M, Graczyk M, Maximov I, Sarwe E L, Ling T G I, Keil M and Montelius L 2002 *Microelectron. Eng.* **61/62** 441
[15] Schift H 2008 *J. Vac. Sci. Technol.* B **26** 458
[16] Mancini D P, Gehoski K A, Ainley E, Nordquist K J, Resnick D J, Bailey T C, Sreenivasan S V, Ekerdt J G and Willson C G 2002 *J. Vac. Sci. Technol.* B **20** 2896
[17] Yang J K W, Cord B, Duan H, Berggren K K, Klingfus J, Nam S W, Kim K B and Rooks M J 2009 *J. Vac. Sci. Technol.* B **27** 2622
[18] Hwy J J, Babin S, Page L, Danilevsky A, Self A, Ueda K, Koshihara S, Wago K, Lee K and Kuo D 2009 *BACUS Photomask Technology Conf.*; *Proc. SPIE* **7488** 68
[19] Babin S, Bay K and Machin M 2010 *Proc. SPIE* **7638** 76380R
[20] Olynick D L, Liddle J A, Harteneck B D, Cabrini S and Rangelow I W 2007 *Proc. SPIE* **6462** 64620J