Benchmarking of 50 nm features in thermal nanoimprint

C. Gourgon^{a)} and N. Chaix

CNRS-LTM, 17 R. des Martyrs F-38054, Grenoble Cedex 9, France

H. Schiff

Paul Scherrer Institut, Villigen PSI 5232, Switzerland

M. Tormen

TASC-INFM 163.5, I-34012 Basovizza-Trieste, Italy

S. Landis

CEA-LETI-Minatec, 17 R. des Martyrs, F-38054 Grenoble Cedex 9, France

C. M. Sotomayor Torres

Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland, Institute for Research and Advanced Studies, ICREA, 08010 Barcelona, Spain, and Catalan Institute of Nanotechnology, Edifici CM7, Campus Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

A. Kristensen, R. H. Pedersen, and M. B. Christiansen

MIC—Department of Micro and Nanotechnology, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

I. Fernandez-Cuesta

CNM—Instituto de Microelectrónica de Barcelona, 08193 Bellaterra, Barcelona, Spain

D. Mendels

National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, United Kingdom

L. Montelius

Division of Solid State Physics, Lund University, P.O. Box 118, S-221 00 Lund, Sweden

T. Haatainen

VTT Micro and Nanoelectronics, Espoo FI-02044, Finland

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The objective of this benchmarking is to establish a comparison of several tools and processes used in thermal NIL with Si stamps at the nanoscale among the authors' laboratories. The Si stamps have large arrays of 50 nm dense lines and were imprinted in all these laboratories in a ~ 100 nm thick mr-18010E film. Other materials, such as mr-17010E, were also tested. Good patterns were obtained and some limitations were identified. Reducing the pressure to 15 bars enables the printing of 50 nm structures without pulling them off. At higher pressures, some bending effects resulting in pattern deformation were observed. It was proven that a pressure of 1.5 bars is sufficient to imprint perfect 50 nm lines. The influence of the antiadhesive layer and mold design has been characterized by the demonstration of pulled off lines in some cases. Moreover, it has been shown that the scatterometry method is particularly useful for the characterization of 50 nm lines and that the residual layer thickness corresponds to the theoretical estimate as long as the lines are well defined. One process was demonstrated which combines high reproducibility with high throughput, achieving a cycle time of 2 min. © 2007 American Vacuum Society. [DOI: 10.1116/1.2794064]

I. INTRODUCTION

Thermal nanoimprint lithography (NIL) is now a commonly used tool at the laboratory scale,¹ and its growing popularity has led to rapidly expanding research, resulting in a large number of laboratories and companies using their own materials, processing conditions, with different tools inside or outside the NAPA project.² While this diversity is welcome to improve the knowledge on nanoimprint technologies, it greatly hampers the definition of standard rules of this technique. The widespread acceptance of NIL as an industrial process requires not only an understanding of the

process and its optimization, but also reproducibility and means to compare between seemingly equivalent technological solutions. In the case of an industrial implementation, one also requires (a) that all critical parameters and sources of variation are controlled, for example, in a six-sigma sense and (b) that the quality of pattern transfer of imprints is statistically independent of the equipment, the laboratory, and the operator. In this context, benchmarking exercises are valuable tools, particularly when the number of floating parameters is limited. A benchmarking has been performed in the framework of the European project "Emerging Nanopatterning Methods" (NAPA),² in order to establish a comparison of the processes used in the laboratories listed in Table I.

^{a)}Electronic mail: cgourgon@cea.fr

TABLE I. Laboratories involved in this benchmarking and the corresponding printing equipment used.

Partner	Equipment	Wafer size (mm)
PSI	Jenoptik HEX03	100
TASC	Weber PW	100
MIC	EVG@ 520HE	100
CNM	OB Ducat 4 in.	100
LU	OB Ducat 6 in.	100
LTM/LETI	EVG@520HE	200
VT	SÜSS NPS 300 (step and repeat)	200

For the benchmarking, 50 nm dense lines were targeted. The same patterns were printed by all the partners, and the outcome was characterized centrally. The following sections describe the experimental details, especially the mold fabrication and imprint conditions. The imprinting results are presented and discussed to highlight some specific rules and conclusions on the NIL processes to print successfully 50 nm structures.

II. EXPERIMENT

To ensure maximum consistency, the molds were fabricated in a single batch at CEA-LETI, and one of these molds was given to each laboratory. They were fabricated by electron-beam/deep UV lithography and plasma etching on 200 mm Si wafers. The patterns are gratings consisting of dense lines with various sizes such as 100/100 and 50/50 nm. All the following results will concentrate on the imprinting of 50 nm dense lines. The patterns are defined in several areas with different surfaces: 1 mm², 400 × 400 μm², and 60 × 60 μm². The gratings are arranged on a 2 × 2 cm² die, as presented in Fig. 1. This electron-beam-written area is surrounded by 350 nm wide dots defined by deep UV lithography in order to distribute the pressure more

FIG. 1. Layout of line arrays on 2 × 2 cm² dies. The numbers 1–12 denote the points at which scatterometry characterization was performed.

FIG. 2. SEM micrograph of 50 nm dense lines on the Si mold.

evenly during the imprint.³ The scanning electron microscopy (SEM) image of Fig. 2 shows the 50 nm dense lines after the Si etching still covered with the resist mask. The Si mold depth is around 110 nm. The lines are slightly underetched. Most of the wafers were cut into 5 × 5 cm² pieces to be compatible with the 100 mm imprint equipments. All the molds are covered with an antiadhesive layer. The material is a commercial liquid solution, “Optool” from Daikin Corporation,⁴ and exhibits a surface energy of 12 mN/m. The molds were imprinted in an mr-I8010E film. The material was provided by Microresist Technology GmbH, Berlin. All the resist films were deposited by spin coating in one laboratory using the same parameters and sent to the participating laboratories. The film thickness is around 100 nm, which should result in a 45 nm residual layer if the conservation of material rule applies. While all the imprints were performed at 170 °C, each laboratory was free to choose the imprint pressure and time. All the imprinted lines were characterized centrally using the same procedure, namely, top-down SEM, cross section SEM, and scatterometry. The latter technique, based on the comparison of ellipsometry analysis of diffracted light to simulation results, was described in previous works,⁵ and its precision and reproducibility was already demonstrated. The ellipsometer spot size was 20 μm diameter, which allows the characterization of the 1 mm² and 400 × 400 μm² line arrays, but not the 60 × 60 μm² ones. The linewidth, here the critical dimension (CD), the residual layer thickness (hr), and the imprinted depth (hi) were measured by scatterometry at several points, as presented in Fig. 1. The measurements 1–5 were performed in the center of each imprinted grating in order to characterize the printing uniformity, whereas measurements 5–12 were dedicated to the characterization of a potential edge bending of the pattern, which would result in a nonuniform residual layer thickness. Points 11 and 12 correspond to the resist thickness outside the grating and therefore to a reference.

III. RESULTS

Typical results of imprinted wafers are presented in Fig. 3. The die containing the 50 nm lines can be seen at the center of the wafer. The diffracted light around this area is due to

FIG. 3. 100 and 200 mm imprinted wafers. The array of 50 nm lines is at the center of the sample.

the 350 nm dots which are present on the all 200 mm wafers and which correspond to the $5 \times 5 \text{ cm}^2$ mold in the case of imprints on 100 mm substrates. An example of 50 nm lines imprinted into a 100 nm mr-I8010E film is shown in Fig. 4. The corresponding scatterometry results are summarized in Table II. They were obtained on one wafer, and the different points correspond to the different measurement locations presented in Fig. 1. The CD is close to 43 nm in the $400 \times 400 \mu\text{m}^2$ gratings and around 50 nm in the 1 mm^2 ones. This difference was also observed on wafers imprinted by other laboratories, and is due to exposure dose nonuniformity during the electron beam lithography step. The imprinted depth value is around 110 nm, demonstrating that the molds are completely filled up in these conditions. The residual layer thickness is close to 53 nm in the case of 40 nm lines, and 44 nm when the CD is 50 nm, which corresponds very well to the theoretical value if one considers that all the polymer flows in the surrounding cavities and that the amount of material is locally constant. The error is a parameter indicating that the fitting of the ellipsometric spectra is very good, and this demonstrates that scatterometry is suitable for the characterization of imprinted nanostructures. It has to be noticed that these results are reproducible and that the same values have been obtained by all the participating laboratories when the imprint process resulted in well defined lines. However, several defects appear, depending on printing conditions, as will be shown in the next section. The

FIG. 4. SEM micrograph of 50 nm dense lines imprinted in an mr-I8010E film.

reproducibility and the throughput on 200 mm wafers were especially analyzed in one laboratory. More than 25 imprints were performed with the same mold without cleaning, on mr-I8010E and NEB22 films. The imprint conditions and the resist thickness were varied, and the processes are summarized in Table III. Some wafers were imprinted for 1 min only with a total cycle time of only 2 min. The additional minute is needed to pump the chamber and to stabilize the wafer temperature. This short cycle time allowing a high throughput of NIL on 200 mm wafers was already demonstrated on larger structures.⁶ Figure 5 shows the 50 nm lines imprinted with these conditions. The imprint quality is as good as the one obtained with a longer process. The scatterometry results are also presented in Table III. They are obtained in the center of a 1 mm^2 grating. It is evident that the imprint results do not depend on the imprint time and the applied pressure in the 1.5–14 bar range. The fast and low pressure process leads to a good filling of the 50 nm patterns, but the same behavior was observed in 100 nm lines. It would be helpful to reduce once again the pressure and the imprint time in order to get a better understanding of the filling properties, but this is not possible with the current equipment. The linewidth is practically constant at

TABLE II. Scatterometry results of the lines shown in Fig. 4.

Measurement	Linewidth (nm)	Imprinted depth (nm)	Residual thickness (nm)	Slope	Error
1	44	108	53	0.75	0.066
2	44	109	52	0.96	0.063
3	43	106	54	0.01	0.078
4	47	111	49	2.11	0.075
5	51	113	43	1.63	0.081
6	51	113	43	1.96	0.069
7	50	113	44	2.73	0.086
8	50	112	44	2.23	0.086
9	51	113	43	1.87	0.075
10	51	115	41	2.67	0.070
11	Outside		160		
12	Outside		160		

TABLE III. Scatterometry results of the lines shown in Fig. 5.

Polymer	Thickness (nm)	Pressure/ imprint time	Linewidth (nm)	Residual thickness (nm)	Imprinted depth (nm)
mr-I8010E	111	7 bars/5 min	50	56	117
mr-I8010E	111	7 bars/10 min	49	59	112
mr-I8010E	111	7 bars/1 min	50	48	110
mr-I8010E	101	7 bars/5 min	50	43	113
mr-I8010E	101	14 bars/5 min	45	50	111
mr-I8010E	101	1.5 bars/5 min	48	45	117
mr-I8010E	156	7 bars/1 min	50	104	114
mr-I8010E	156	7 bars/5 min	51	101	115
NEB22	200	7 bars/1 min	49	148	116
NEB22	200	7 bars/5 min	49	147	116

49 ± 2 nm, and the imprinted depth always corresponds to the mold depth, proving the full filling of the cavities. Only the residual layer thickness changes with the resist thickness. The graph of Fig. 5 presents the residual layer thickness as a function of the initial polymer thickness. All the experimental points correspond to the processes listed in Table III. This graph demonstrates that the experimental residual layer thickness is in good agreement with the theoretical one depending only on the initial film thickness as long as it is thick

enough to guarantee mold filling. These results show that imprint processes are now mature in terms of reproducibility and throughput capability for a feature size of 50 nm. A step and repeat process has been also demonstrated on 200 mm wafers, as shown in Fig. 6. The mold is heated then pressed into the polymer and cooled down before automatic demolding and moving to the next die position.^{7,8} Some good 50 nm lines were obtained, albeit with poor homogeneity. The reason is the mold size, which is too large to guarantee a uniform pressure on the NPS300 equipment.

IV. DISCUSSION

The results presented in the last section demonstrate that the same patterns were obtained in all the participating laboratories when the lines are well imprinted. However, some defects were observed by most partners. These are discussed below to help define some rules for the imprint of 50 nm structures. First, the lines were often pulled off during the demolding step, but on 100 mm wafers only, and this effect is independent of the demolding direction, which can be parallel or perpendicular to the lines. This is due to the difference of the demolding conditions. In both cases, a razor blade is introduced manually between the wafers, and while the distance between the blade and the patterns is 100 mm in the case of 200 mm wafers, it is only 20 mm in the case of 5×5 cm² molds imprinted on 100 mm wafers. The bending of the lines is therefore more important in the second case, and the stress becomes so high that the lines brake and stick

FIG. 5. Top: SEM micrograph of 50 nm dense lines imprinted in a 2 min process. Bottom: Corresponding scatterometry results.

FIG. 6. 200 mm wafer and 50 nm lines imprinted with a step and repeat process.

FIG. 7. Schematic description of the influence of the blade/pattern distance. (a) Pulled off lines on 100 mm wafer. (b) Lines imprinted with the same mold covered by a fluoro-silane antiadhesive layer deposited by vapor phase.

to the mold surface. An example is shown on the SEM image of Fig. 7(a). One mold was cleaned and a fluoro-silane antiadhesive layer was deposited by chemical vapor deposition.⁹ The same imprint process was performed and lead to the well imprinted lines shown in Fig. 7(b). The reason of this difference is not fully understood at present since both antiadhesive layers have approximately the same surface energy. Nevertheless, this could prove once more that liquid phase

coating is not the most appropriate solution to decrease the mold surface energy, as it was already claimed in Ref. 10.

The other important parameter identified for these imprints is the applied pressure. High pressures in the range of 50–100 bars are normally used in thermal NIL. Yet, in this study the pressure had to be reduced in order to print correctly the 50 nm lines. This is illustrated in Fig. 8. The lines printed at 40 bars are completely pulled off, which is not due to sticking problems because sticking effect would lead to a SEM observation, as presented in Fig. 7, and their aspect is totally different. It is clear that the polymer flew down during the imprint. The same behavior was observed in all laboratories using different tools. When the pressure was reduced to 15 or 10 bars, the lines were well printed. Furthermore, even at 1.5 bars it was shown that the mold cavities are filled. The behavior obtained at 40 bars is attributed to a mold bending during the printing step or to an excessive stress at the bottom of the patterns.¹¹ It can be observed on the pictures that the lines were first printed. Their position is still visible, but the pressure was so high that strains were induced, leading to a mold deformation. This resulted in a new and uncontrolled polymer flow and therefore to the de-

FIG. 8. Influence of the pressure on the imprint of 50 nm lines.

struction of the printed lines. It has to be noticed that both effects, sticking on to mold and deformation of the lines due to the high pressure, depend on the polymer chemistry since the results are better when using the mr-I17010E polymer. This difference is still under investigation. This benchmarking demonstrates that the printing of nanostructures needs special rules and precautions because these problems observed with the 50 nm lines do not occur for 100 nm lines.

V. CONCLUSION

This benchmarking successfully compared the thermal NIL processes and equipments of the participating laboratories. It demonstrated that special rules have to be considered for the printing of 50 nm lines. A lower pressure is particularly needed with this mold design. A successful and reproducible printing of dense 50 nm lines has been achieved, showing that some processes are sufficiently mature and could be ready for industrial production development. Besides, they are compatible with a high throughput based on cycle times as short as 2 min for 200 mm wafers. Scatterometry has been shown to be a useful metrology technique for thermal NIL of 50 nm lines.

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