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Nanoimprint lithography processes on 200 mm Si wafer for optical application: Residual thickness etching anisotropy

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It is well known that one limitation of thermal nanoimprint lithography is the difficulty to imprint simultaneously nano- and microstructures because of the resulting different residual layer thicknesses, which induce a very poor control of the pattern sizes during the etching steps. Line gratings with densities varying from 1 to 15 have been imprinted on 8 in. wafers. The residual thickness varies from 38 to 158 nm. Different plasma chemistries have been studied for the etching of the residual layer. The patterns have been characterized after the imprint and the etching steps by scatterometry. The results show that some chemistries are very promising for the control of the patterns during the etching step. A O₂/C₁₂/Ar process has been particularly studied, and it has been demonstrated that it presents a very high anisotropy, which allows the use of long etching times in order to remove the residual layer in gratings with various densities with no variation of the critical dimension. © 2007 American Vacuum Society. [DOI: 10.1116/1.2801878]

I. INTRODUCTION

Thermal nanoimprint lithography¹ (NIL) is a very promising nanopatterning technique for various domains of applications, especially for optical devices. Nevertheless, several issues still limit its use at an industrial scale. One of the important drawbacks of thermal NIL is the control of the residual thickness (hr) of polymer remaining at the bottom of the patterns after the imprint.² It is well established now that patterns with various densities and sizes result in a nonuniform residual thickness since the polymer flow is mainly driven by the ratio between the mold cavity volume and the pressed material volume.³ This hr distribution is not a problem for applications using directly the imprinted polymer as a functional material. However, many applications require a transfer of the resist patterns into the underlying substrate. This transfer is usually done by plasma etching. The residual thickness is etched first. The etching time has to be long enough to guarantee a complete etching of hr even for large values. As a consequence this etching step is completed first, where hr is thinner. This may lead to a critical dimension (CD) change for printed feature due to the horizontal etch rate. Therefore the control of imprinted feature size with various densities may be very tricky. In this article we present a study of the control of the pattern size depending on the plasma chemistry during hr etching process, and a high anisotropy process is demonstrated. It is shown that a high control of the pattern size is obtained in structures with densities varying from 1 to 15.

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II. EXPERIMENTAL DETAILS

Stamp has been manufactured by deep ultraviolet optical lithography ($\lambda=248$ nm) with a 450 nm thick positive resist (UV5) from Rohm & Haas Company. After the development, the patterns are transferred into the silicon using high density plasma etching. Stamps were coated with a fluorocarbon-based antisticking layer, Optool DSX (Daikin corporation⁴), to reduce the surface free energy of the mold from 60 mJ/m² down to 11 mJ/m².

Figure 1(a) shows optical and scanning electron microscopy (SEM) views of 8 in. silicon stamps containing more than 400–180 nm deep optical devices made of a 250 nm dense line arrays. Another 260 nm deep mold with line size ranging from 200 nm up to 1 μ m and filling factor ranging from 1 to 15 was used in order to point out the influence of the feature density. The complete mold design is presented in Fig. 1(b).

Printing processes were performed on 8 in. wafers in an EVG[®]520HE system.⁵ The maximum force that can be applied by the piston is 40 kN, which is equivalent to a pressure of 12.7 bars over an 8 in. wafer. The printing process is performed under vacuum (7×10^{-2} mbar) with typical process conditions set at 5000 N, 130 °C, and a printing time set at 5 min (Fig. 2). A 200-nm-thick Sumitomo NEB 22 resist film was coated on a silicon substrate with native oxide. This resist is a high resolution, chemically amplified resist first designed for electron beam lithography. We have already shown⁶ that this resist film is suitable for hot embossing processes, and thanks to its etching resistance, can be used to transfer the printed pattern into the substrate. Prior to the printing process, the resist film was first annealed at 110 °C for 2 min in order to remove the residual solvent. The resist is a blend of polymers based on poluhydroxysty-

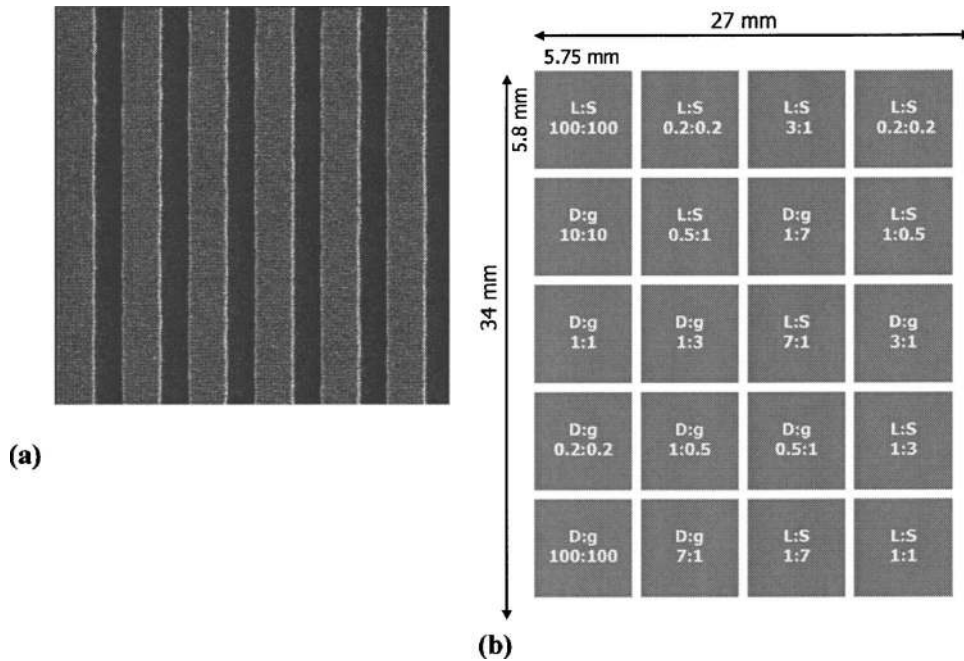


FIG. 1. (a) First mold: Si wafer covered with 250 nm dense lines; (b) second mold: Si wafer with ~ 20 dies presenting various pattern sizes and densities.

ren, and it is a thermoplastic polymer with a glass transition temperature around 80 °C. The etching behavior of this resist is therefore similar to the one of standard NIL materials.

A residual resist layer has been etched using several plasma processes in an Applied Materials IPC reactor (Table I). The main etching time t_0 was determined using end point detection. As soon as residual thickness (hr) is etched, emission of the CO bond decreases since a silicon surface appears, indicating that the etching step is finished.

To ensure a fine characterization of the etching process and its optimization, a nondestructive metrology technique should be used. As already shown⁷ scatterometry appeared to be suitable since the whole geometry (height, CD, sidewall angle, hr) may be determined.⁸ The diffraction figure was computed using rigorous electromagnetic simulation code [MMFE (modal method by Fourier expansion)⁹]. We used a library based approach for the extraction of the geometrical parameters from ellipsometric parameters measured on specific targets consisting on gratings larger (5 mm)² than the ellipsometer spot (typically close to 50 μm). Therefore this measurement may be seen as an in line characterization.

III. RESULTS AND DISCUSSION

The lines imprinted with the two molds are shown on Fig. 2 and the CD was measured by scatterometry. The results show that the imprinted CDs are very close and independent of the position on the wafer (Fig. 3). For the same pattern, the difference between the CD values is less than 5%. The homogeneity of the CD values is good for different L (line size)/ S (spacing) ratio studied: 1/0.5; 0.2/0.2; 1/1; 0.5/1; 1/3; 1/7. The homogeneity control is possible with the very good imprint pattern quality.

The etching of the residual layer (hr) of polymer is the key point of the complete development of a NIL process for future industrial applications. It has been demonstrated that

for a given pattern geometry, the residual layer is homogeneous on large surfaces such as 8 in. wafers,¹⁰ but some small variations can also appear, and a etch process insensible to these differences would be of benefit to industrial processes. The key point of the hr etching is therefore the anisotropy of the process. Two etch rates can be determined during the plasma etching: one corresponds to the vertical etching and to the value commonly measured, and one is representative of the lateral etching. During the plasma etching process a time t_0 is needed to open the residual layer in the patterns having the smallest hr. If the next etching step is performed directly, only these patterns will be transferred into the substrate because some resist remains at the bottom of the other patterns. It is therefore necessary to increase the time of the hr etching to t_1 to get a complete opening of all the patterns. If the hr etching process is anisotropic, all the patterns will be transferred to the substrate with a good control of their size. That means that the etch rate in the lateral direction is very small. In the case of an isotropic process, the width of the first patterns will be changed during the overetching time because the lateral etch rate becomes higher as soon as the amount of resist that can be etched vertically decreases.

The anisotropy of several etching processes has been characterized. The imprinted patterns are 240/260 nm lines, as shown on the SEM picture of Fig. 4. The residual layer is 110 nm thick, and the pattern height is 180 nm, which is a small resist budget useful to characterize the profile fidelity during the hr etching. Five plasma chemistries have been tested. The etching rate was first measured for each process on a flat polymer surface to determine the etching time needed to open 110 nm. Then the patterned wafers were etched using this time and were characterized by SEM. The linewidth was measured at the top and at the bottom of the line to control the CD and the fidelity of the vertical profile.

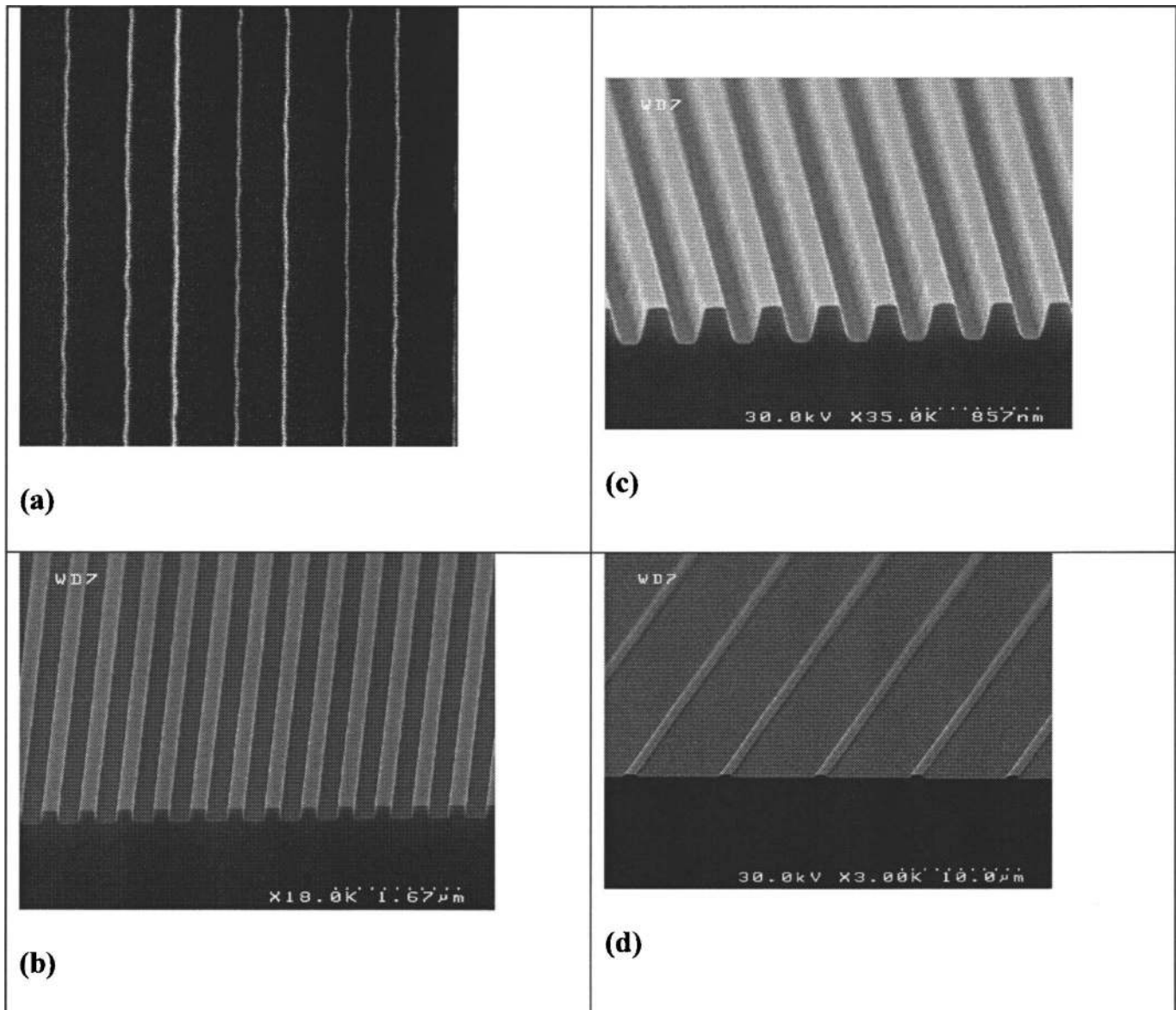


FIG. 2. [(a) and (b)] Optical and SEM images of the 250 nm dense line imprint. The height of the feature is 180 nm. [(c) and (d)] SEM images of the second mold imprint for two samples: 0.2/0.2 and 1/7 ratios.

The resist height was also measured. The five plasma chemistries are the following: (1) $\text{O}_2/\text{Cl}_2/\text{Ar}$ (3/4/3); (2) CF_4 ; (3) $\text{CF}_4/\text{CH}_2\text{F}_2$ (4/3); (4) HBr/O_2 (6/1); (5) HBr/O_2 (3/1).

Figure 4 presents the corresponding SEM pictures. There is no picture for the process 5 since the higher content of oxygen leads to a huge lateral etching, and the patterns were completely stripped during the hr opening.

TABLE I. Linewidth (CD) and height measured after the imprint and hr etching processes.

	Imprint	$\text{O}_2/\text{Cl}_2/\text{Ar}$ (3/4/3)	CF_4	$\text{CF}_4/\text{CH}_2\text{F}_2$ (4/3)	HBr/O_2 (6/1)
CD top	240	210	200	130	210
CD bottom	240	250	210	315	230
Ei	180	180	180	154	180
Vertical etch rate		3 nm/s	2.3 nm/s	0.6 nm/s	1.2 nm/s

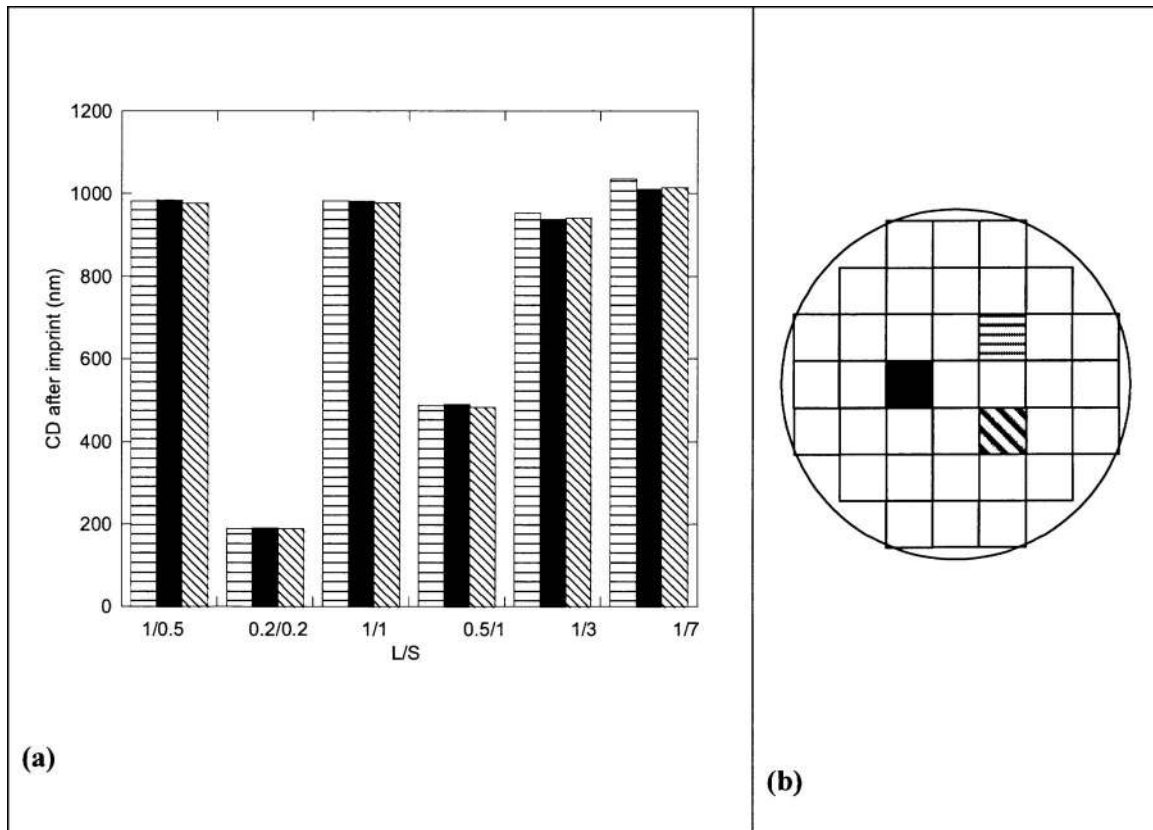


FIG. 3. (a) Measurement linewidth (CD) for several L/S ratios (1/0.5;0.2/0.2;1/1;0.5/1;1/3;1/7) for three chips on 200 mm wafer. (b) Mapping of the scatterometry measurements on the 200 mm wafer.

It is clearly shown that the CF_4/CH_2F_2 process has a too low etch rate and leads to a very poor control of the profile due to etch products which are redeposited on the sidewalls during the etching. The values of the corresponding linewidth and height are given in Table I.

The $O_2/Cl_2/Ar$, CF_4 , and $HBr/O_2(6/1)$ processes lead to better profiles and the resist height is still 180 nm after the etching. This demonstrates that the vertical etch time is well controlled. But some differences still appear. Despite a vertical sidewall, the lines etched with the CF_4 process present a smaller CD; this illustrates that the process is homogeneous,

but not anisotropic enough. Finally, the $O_2/Cl_2/Ar$ and $HBr/O_2(6/1)$ processes exhibit a good anisotropy. Some corner rounding appears at the top of the line, but the vertical sidewall allows a direct transfer of the structures with a good control of the linewidth. The $O_2/Cl_2/Ar$ process shows a higher etch rate (3 nm/s compared to 1.2 nm/s) and would perhaps be preferred for industrial applications.

The $O_2/Cl_2/Ar$ process was chosen to study the etching anisotropy in patterns with various densities. This choice is based on the previous results since this chemistry exhibits the best control of CD for one kind of structures. Several

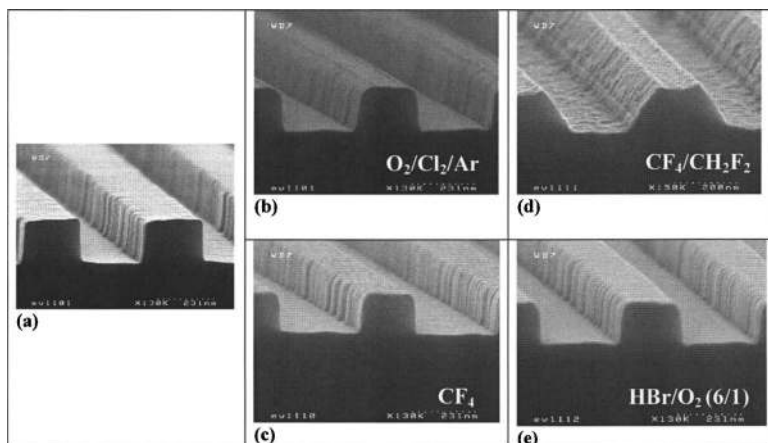


FIG. 4. (a) Images of 200 nm dense lines imprinted in NEB resist; [(b)–(e)] residual layer etching using different plasma chemistries.

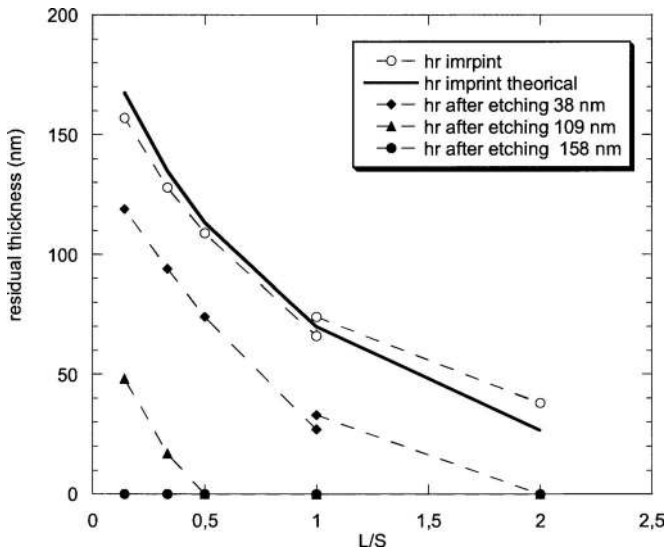


FIG. 5. Results of the mapping measurements: study of the residual thickness (hr), hr as a function of the ratio L/S for experimental and theoretical imprints and after three etching levels (38, 109, and 158 nm) for five L/S ratios (1/0.5; 0.2/0.2; 1/1; 0.5/1; 1/3; 1/7).

wafers have been imprinted using the mold with filling densities ranging from 1 up to 15. The residual thickness has been measured by scatterometry in several dies depending on the L/S ratio. The experimental results are presented on Fig. 5. The line is defined by the theoretical values of hr, determined by the conservation of the polymer volume which flows to the mold cavities. This leads to the following equation: $hr = \text{initial polymer thickness} - \text{mold depth} (1/(1+L/S))$.

It is clear on Fig. 5 that the experimental hr is in good agreement with the theoretical one. The wafers have been etched in order to remove the residual thickness using the O₂/Cl₂/Ar process. Three different etching times have been used. The first one corresponds to the time needed to etch 38 nm, which is the lowest hr measured in the 1/0.5 μm lines. The residual thickness is therefore equal to zero only in this grating. The second is defined to etch 109 nm, and the last one is long enough to remove the largest hr of 158 nm. In this last case, the residual thickness is completely etched in all the patterns, but an overetch time was therefore applied to the gratings with a L/S ratio higher than 0.14. The resulting residual thickness has been characterized by scatterometry again after the etching process, and the results are summarized on Fig. 5. The hr values are in good agreement with the expected ones defined by the imprint hr minus the etched thickness, 38, 109, or 158 nm. In the case of a 158 nm etching, the overetching time corresponds to a virtual etching of 120 nm in the case of $L/S=2$. That means that an isotropic etching process would lead to a complete stripping of the resist during the overetching. The CD was also measured after the etching step by scatterometry and compared to the imprinted CD on Fig. 6. With anisotropic etching process, one would expect no variation of the CD after the etching step, and this perfect behavior is illustrated by the dashed line. The experimental points corresponding to the three different etching times are reported on the graph, and it appears

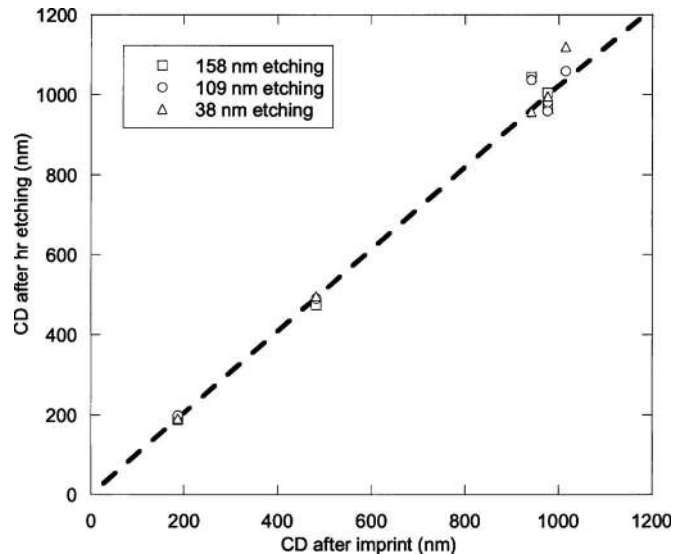


FIG. 6. Measurement of the linewidth (CD) after three etching levels (38, 109, and 158 nm) compared to the CD measurement after imprint for three widths (0.2, 0.5, and 1 μm).

that there is a very good agreement between the CD achieved after the imprint and the etching step. This result demonstrates that the O₂/Cl₂/Ar process is highly anisotropic and that an overetching time guarantees nevertheless the control of the CD. This process is a potential solution for the pattern transfer in structures with nonuniform residual thickness. The remaining resist thickness after a 158 nm etching step is presented on Fig. 7. The theoretical value is defined as follows: when the etching time corresponds exactly to the removing of the residual layer, the remaining thickness is equal to the 260 nm mold depth. This is observed only for $L/S=0.14$. As long as an overetching occurs for higher L/S , the CD is not changed because of the high anisotropy, but the vertical etching continues and decreases the resist thickness.

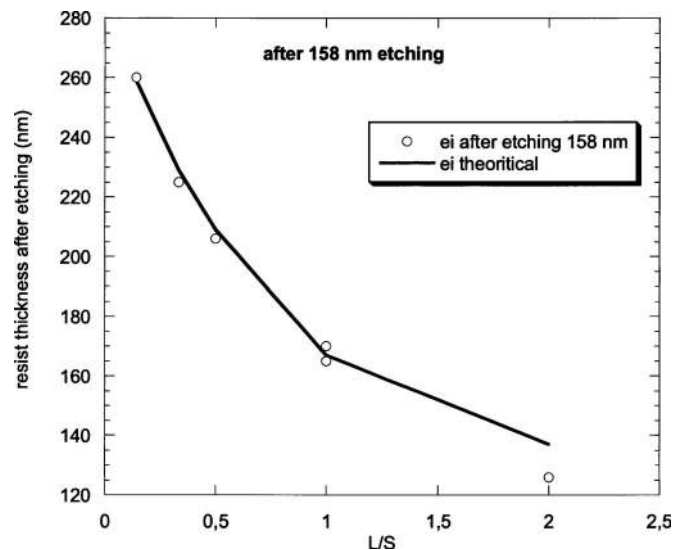


FIG. 7. Experimental and theoretical values of the resist thickness as a function on L/S .

The final value should then correspond to the difference between the mold depth and the overetched thickness. As the overetching (vertical etching) time corresponds to 120 nm for $L/S=2$. The final resist budget is then 140 nm only. The graph shows that the experimental resist thickness is in good agreement with the expected one. This effect is a limitation to the use of the anisotropic process since the reduction of the resist budget for the following transfer into the underlying substrate limits the possible etching depth. A hard mask can be nevertheless used to overcome this drawback. Once again a trade off has to be done between the resolution and the mold depth allowing a high transfer depth.

IV. CONCLUSION

A study of the residual layer etching has been presented and it has been shown that special plasma chemistries are of benefit to the pattern transfer, compared to a pure oxygen process which usually requires a very small hr value. A $O_2/Cl_2/Ar$ plasma process has been developed and its high anisotropy has been demonstrated. It has been shown that overetching times can be used with no variation of the pat-

tern sizes, and that this high control of the features allows a perfect transfer of patterns with various residual thicknesses induced by different densities. This etching process could be a solution for the well known limitation of thermal NIL, and it was proven that it allows the imprint and etching of nano- and microstructures simultaneously.

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