New Organic Photo-Curable Nanoimprint Resist «mr-NIL210» for High Volume Fabrication Applying Soft PDMS-Based Stamps

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Herein, we report on a newly developed and commercialized organic photo-curable Nanoimprint Lithography (NIL) resist, namely mr-NIL210. Since this new NIL resist follows an innovative design concept and contains solely specific monomers with a characteristic chemistry and molecular design, an extended longevity of applied polydimethyl siloxane (PDMS) stamps is enabled addressing a crucial key metric for industrial high-volume manufacturing processes. Moreover, the mr-NIL210 is characterized by a negligible oxygen sensitivity of the curing chemistry, outstanding film forming and adhesion performances as well as excellent plasma-based dry etch characteristics for various substrate materials like silicon, aluminum, sapphire, titanium, etc.

Keywords: nanoimprint lithography, PDMS-based stamps, high volume nanofabrication, PDMS compatibility

1. Introduction

Nanoimprint lithography (NIL) has emerged as a widely used parallel patterning technique for the fabrication of various functional nano-patterned features in scientific and industrial devices and is in particular well-suited for high throughput and low-cost nanofabrication processes addressing a variety of different applications such as nanophotonic devices, bit-patterned media, light emitting diodes (LED), but also (bio)sensors and lab-on-chip devices [1, 2, 3].

In this regard, especially soft NIL techniques using flexible PDMS-based stamp materials gain much interest due to a couple of very beneficial advantages compared to hard and rigid stamps typically employed in conventional NIL processes [4, 5]. Most strikingly, PDMS-stamps can be used for a fast full-wafer patterning of large wafers in one single imprint step [6].

Due to the flexibility of the PDMS stamp imprint defects originating from particles on the substrate surfaces are much less critical as they can be easily overprinted in a way that the overall defectivity remains still low [7].

Besides, the flexibility of the PDMS stamps enables the patterning of non-planar and other arbitrarily shaped substrate surfaces opening up completely new application fields for soft NIL [8]. However, the great majority of the generic resist materials for soft NIL still suffer from a rather limited compatibility to PDMS-based stamps. This originates mostly from the fact, that resist components like monomers often reveal non-negligible propensity to permeate into the PDMS matrix of the stamp [9]. As a result the crosslinking of those resist components during UV expose results directly in the formation of an interpenetrating network at the interface between the stamp and the resist, so that the PDMS stamp and the NIL resist are strongly tied to each other. Therefore, imprint defects like complete tear-offs and/or cohesive failures are rather likely to occur during the stamp separation step. Even more important, the ripped off and cured NIL resist material remain in the stamp cavities and cannot be easily removed by a cleaning process, so that the stamp is mostly irreversibly damaged. This effect also strongly reduces the stamp life-time which is in turn very detrimental for a utility in high-volume production processes.

2. Material development and evaluation

We have developed the new organic photo-curable soft nanoimprint (P-NIL) resist, namely mr-NIL210, that features a significantly improved PDMS stamp compatibility rendering thus an highly extended stamp longevity. This was basically accomplished by engineering the resist formulation in such a way that only special monomers featuring a special molecular architecture were employed and by admixing effective initiators and specific additives.

2.1. Film forming performance and characteristics

By applying standardized versions of the mr-NIL210, thin films can be prepared via the spin-coating technique leading to adjusted film thicknesses of 100, 200 and 500 nm, respectively. Other film thicknesses can be also obtained in the range between 100 nm and several microns by adjusting the amount of monomer in the formulations and/or by varying the spin-speed.

Typically, mr-NIL210 is highly compatible with many commercialized adhesion promoters like e.g. mr-APS1 (*micro resist technology* GmbH, Germany) or OmniCoat™ (MicroChem Corp., US) but can be also employed in the frame of bi-layer systems using adequate organic transfer layers materials like LOR™ (MicroChem Corp., US) or UL1 (*micro resist technology* GmbH, Germany) for example.

Prepared films with mr-NIL210 reveal excellent film forming performances and adhesion characteristics as well as very good film thickness homogeneities over the entire film area over the course of at least 24 hours. Moreover they feature a very low tendency for an edge bead formation. Undesired film forming anomalies like dewetting effects, striations etc. are negligible. Exemplarily, photographic images of prepared films of mr-NIL210 onto a Si wafer are presented in Figure 1.

a) b)

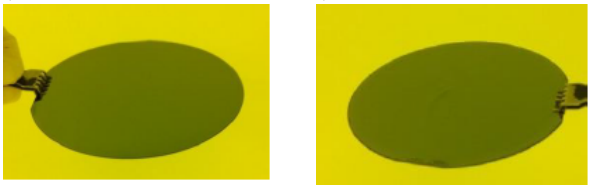


Fig. 1. Photographic images of a defect free film using mr-NIL210 onto a Si wafer. a) directly after film preparation and b) 24 hours after film preparation.

2.2 PDMS compatibility and imprint performance

As already mentioned above, the PDMS compatibility of the NIL resist is strongly dependent on the probability of the resist components to diffuse into the PDMS stamp matrix. Therefore, all employed resist components of mr-NIL210 like e.g. monomers feature an intrinsically low tendency to diffuse into the PDMS matrix of the imprint stamp. However, as the diffusion process is also a function of time, we conducted an empirical evaluation study, in order to assess the time-dependency of the resist material to permeate into the PDMS stamp. To this end, imprint experiments were performed in such a way that we kept the PDMS stamp in contact with the uncured mr-NIL210 material over an extended period of time, i.e. 6 min., 60 min., and 165 min., respectively, before we cured the NIL resist by UV illumination in a standard mask aligner (MA6 from Süss MicroTec, Germany) and removed the PDMS stamp from the imprinted patterns. In Figure 2 corresponding SEM images of the imprinted pillar arrays are depicted.

The absence of any discernible imprint defect in all recorded SEM images is a strong indication that the resist components and in particular the monomers of mr-NIL210 have not substantially permeated into the PDMS stamp which in turn means that their propensity to diffuse into the working stamp made of UV-curable PDMS KER-4690 (Shin-Etsu Chemical, Japan) is intrinsically very low. This inference is further corroborated by the finding that the pillar dimensions, i.e. the pillar height as well as the pillar widths remain nearly constant irrespective of the contact time of the stamp and the uncured resist material. However, in this regard we have to point out, that this result is achieved under pressure-free conditions, in which the filling of the cavities is accomplished only by the virtue of the capillary forces.

In order to further substantiate the high PDMS compatibility of mr-NIL210 and to further evaluate its suitability for high volume fabrication processes, a series of 30 consecutive imprints was performed. In all imprints the UV intensity was 50 mW/cm^2 as the curing chemistry of mr-NIL210 typically requires a minimum illumination intensity of 50 mW/cm^2 or higher in order to render a sufficient fast cross-linking of the monomers – particularly when the feature size and the dimensions of the imprinted patterns and/or the residual layer are smaller than approx. 100 nm.

However, the mr-NIL210 resist can be also cured by applying illumination intensities lower than 50 mW/cm^2, but requires then significantly higher exposure doses than 1000 mJ/cm^2, which is achievable by a prolonged exposure time.

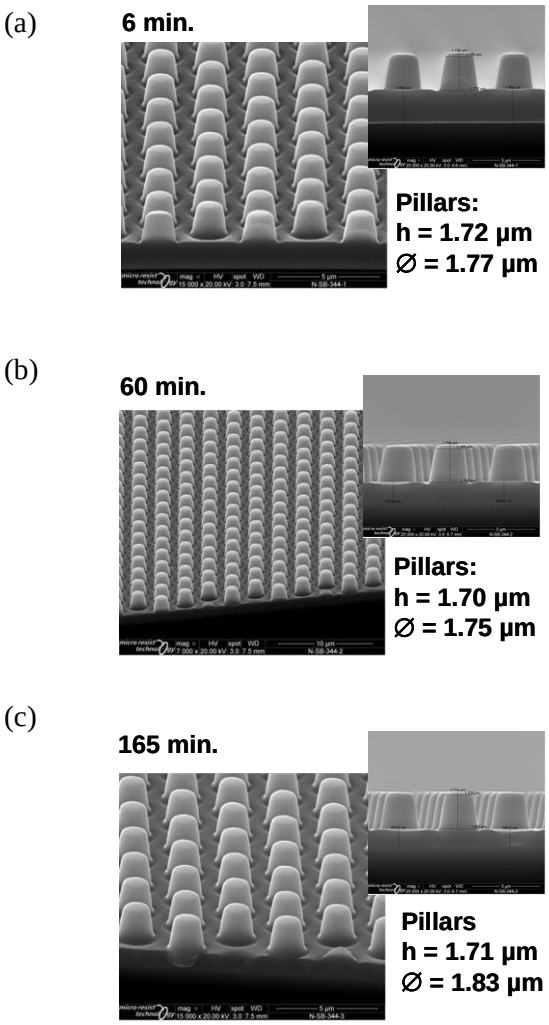


Fig. 2. Tilted SEM images (left side) and cross-sectional SEM images (right side) of imprinted pillar arrays, imprinted with stamp-resist contact time of 6 min. (a), 60 min. (b) and 165 min. (c), respectively. Imprint parameters: UV-dose: D = 1000 mJ/cm^2; cavity filling by capillary forces; imprint stamp prepared by using UV-PDMS KER-4690.

The pillar arrays of the first imprint and the 30th consecutive imprint into mr-NIL210 were analyzed via SEM measurements. Corresponding SEM tilted view and side view images of the first imprint and the 30th imprint are presented in Fig. 3. They clearly show flawlessly imprinted pillar arrays exhibiting no indications of imprint defects or other imprint anomalies. Moreover, as the pillar dimensions also remain constant and display no relevant differences we reason logically that the amount of resist components that permeate into the PDMS within the 30 consecutively conducted imprints is supposed to be negligible.

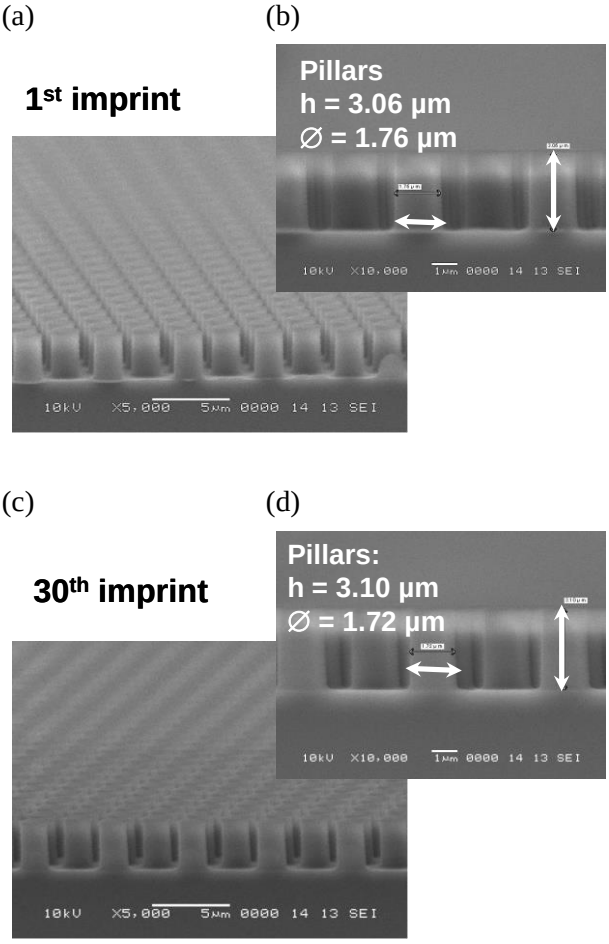


Fig. 3. SEM tilted view images (a) and (c) and side view images (b) and (d) of an imprinted pillar array applying mr-NIL210 onto a Si wafer coated with a thin mr-APS1 layer as adhesion promoter; imprint parameters: stamp material UV-PDMS KER-4690 stamp, imprint at RT, UV exposure dose: 1000 mJ cm^{-2} (20 s upon 50 mW cm^{-2}), (a) and (b) show SEM images of the first imprint, while (c) and (d) exhibit the imprint result of the 30th consecutive imprinted pattern.

Besides, the imprint performance of mr-NIL210 was further evaluated by imprinting a large pillar array featuring pillars with an aspect ratio > 2 and a top pillar diameter of 500 nm. Here, the imprint is more challenging as the contact area between the stamp and the resist is markedly larger. However, the SEM tilted view and side view images displayed in Figure 4 clearly show that no imprint defects can be discerned indicating

Table 1. Dry etch characteristics of mr-NIL210 in standard etch processes for industrially relevant substrates

Substrate	RIE Tool	Gas Flow Rate [sccm]	ICP (*Platen) Power [W]	Platen Temp. [°C]	Chamber Pressure [mTorr]	Substrate Etch Rate [nm/min.]	Etch Selectivity (Substrate : Resist)
Silicon	STS ICP	C_4F_8 /SF_6 (90/30)	600	20	9.8	150	2.50 : 1
Borosilicate glass	OI BP80	CHF_3 (20)	100	20	15	65	0.28 : 1
Sapphire	OI ICP 180	BCl_3/Cl_2 (90/10)	1200 (*200)	20	12	33	0.56 : 1
Titanium	OI System 100	$SiCl_4$ (18)	250	22	4	34	0.80 : 1
Cured resist ash rate	GI Plasma	O_2 (240)	100	20	135	n/a	63 nm/min.

thus the excellent PDMS compatibility of mr-NIL210.

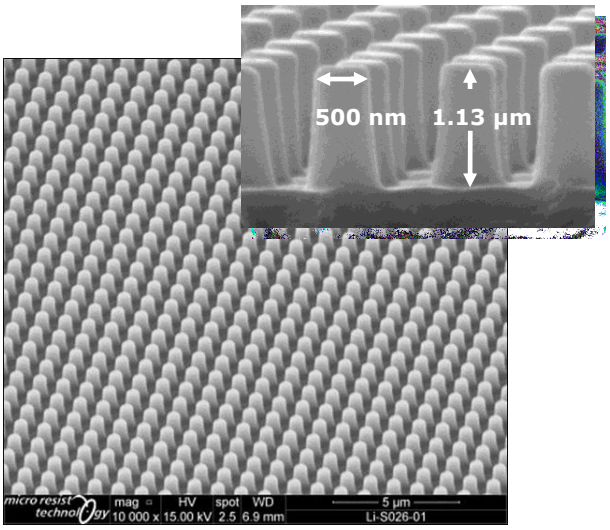


Fig. 4. Tilted view image (left side) and cross-sectional image (right side) of imprinted pillar array, imprint parameters: UV dose: D = 1000 mJ/cm^2; cavity filling by capillary forces; imprint stamp prepared by using UV-PDMS KER-4690, imprint at RT.

2.3 Etch characteristics

2.3.1 General dry etching of mr-NIL210

mr-NIL210 was originally developed for being used as NIL resist in subsequent pattern transfer into the applied substrates materials via conventional plasma dry etching processes. In order to demonstrate the dry etching capability of the novel mr-NIL210 resist, we have conducted a comprehensive plasma etching study for selected industrially relevant substrate materials, like e.g. silicon, borosilicate glass, sapphire, and titanium. Established dry etching processes based on different plasma chemistries as they are typically applied in standard pattern transfer processes dedicated to each substrate material have been performed. The different dry etching processes were done on flat and non-structured thin films of mr-NIL210 and the etching rate was compared to the etching rate of the pristine substrate materials under equal process conditions. The results of this comprehensive dry etching study are summarized in Table 1. As can be seen, mr-NIL210 shows an appropriate behavior during dry etching, e.g. an etch selectivity of silicon to resist of 2.5:1 can be calculated. It has to be mentioned that the depicted etch selectivity of mr-NIL210 for the different plasma etching processes do not demonstrate the maximum possible dry etching resistance of mr-NIL210 since there was no optimization of the etching parameters conducted concerning maximum dry etching performance. Furthermore, it is obvious that the etching performance of a NIL resists in addition highly depends on the density

and size of the imprinted structures as well as the overall condition of the etching chamber and tool. Hence, the data shown in Table 1 depicts a general rule of thumb and the end user is able to further enhance the etching selectivity of mr-NIL210 by adjusting the processing parameters during the pattern transfer properly.

With the conduction of these general dry etching investigations it is demonstrated, that the mr-NIL210 resist shows meaningful etching behavior under different conditions and, hence, is highly suitable for direct pattern transfer processes.

2.3.2 Pattern transfer process of mr-NIL210 into silicon

To demonstrate a complete lithographic pattern transfer process into silicon, we have selected a dense pattern array of imprinted pillars with 175 nm in diameter and a height of 300 nm as shown in Figure 5 top left. The nanopillar imprints have been fabricated in a step-and-repeat process using a custom built NIL stepper with 356 nm LED exposure.

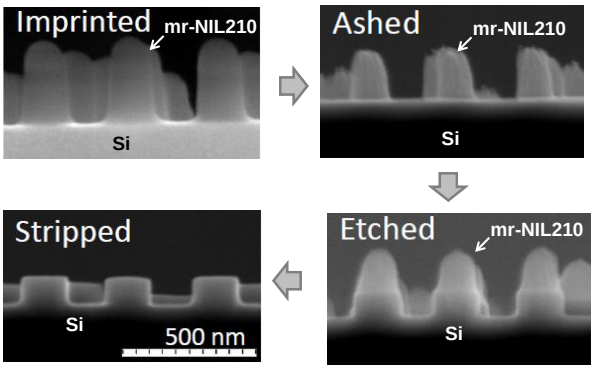


Fig. 5. Cross sectional SEM imaging of a complete pattern transfer process into silicon of an imprinted mr-NIL210 nanometer sized dense pillar array; imprinted pillars (top left), ashed residual layer by 40 s of oxygen plasma (top right), pattern transfer into Si using 40 s of C_4F_8/SF_6 (bottom right), and finally wet chemically stripped resist using piranha etch for 2 min. (bottom left).

Figure 5 gives an overview on the performance of the newly developed resist mr-NIL210 during such a pattern transfer process. The top right cross sectional SEM image in Figure 5 shows the remaining structures after successful removal of the residual layer. The bottom right SEM image demonstrates the excellent pattern transfer fidelity of mr-NIL210 during Si dry etching using a combination of C_4F_8 and SF_6 gas. Pattern transfer of imprinted mr-NIL210 pillars into Si was conducted for 40 s during this experiment following the etching recipe for Si as summarized in Table 1. It can be seen that resist residues remain on the top of the already transferred pillars after silicon etching. Finally, the last step of the pattern transfer process is a stripping of these resist residues after successful pattern transfer using a chemical wet etching with piranha solution (sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), 3:1 ratio). The cross sectional SEM image in Figure 5 bottom left indicates that there are no residues after the stripping process and that the cured mr-NIL210 resist can be completely removed by such a wet chemical stripping performed after plasma etching.

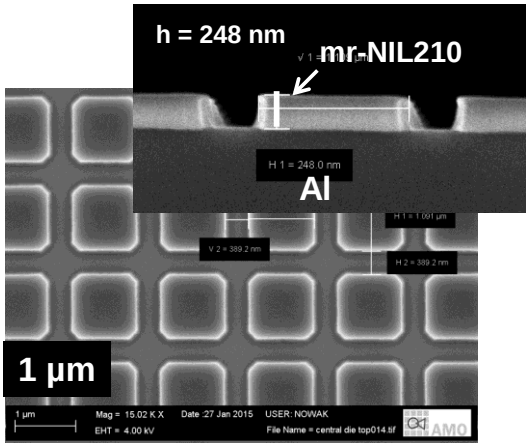
2.3.3 Pattern transfer process of mr-NIL210 into aluminum

Of particular industrial interest is the dry etching behavior of a NIL resist during etching of metals like e.g. aluminum. We have selected an octahedron pattern for this investigation which was imprinted into mr-NIL210 via surface conformal imprint lithography (SCIL) [10, 11]. This special imprint lithography process is particularly based on the use of PDMS originated working stamp derivatives which makes it in particular highly suitable as imprint technology for mr-NIL210.

The SEM images in Figure 6 (a) illustrate conducted imprints on Al. The inlay of Figure 6 (a) exhibits a cross sectional SEM image of the imprint from which an imprinted pattern height of 248 nm can be calculated. Figure 6 (b) gives an tilted SEM side view of the finally transferred patterns into Al using BCl_3 plasma etching in an ICP100 reactive ion etching (RIE) tool (Oxford Instruments). As can be seen, the aluminum structures show an excellent sidewall accuracy rendering the mr-NIL210 resist as highly suitable for being applied as etch mask for aluminum. Based on the measured initial imprinted pattern height of mr-NIL210 an etching selectivity of resist to aluminum of 1:1.4 can be calculated.

In Figure 7 an area of about 15 x 20 micron of the finally etched aluminum structures is presented recorded via SEM imaging, demonstrating the excellent lateral accuracy of mr-NIL210 during BCl_3 RIE into aluminum on large area. The aluminum etching process was conducted till complete consumption of the imprinted mr-NIL210 dry etch mask.

(a)



(b)

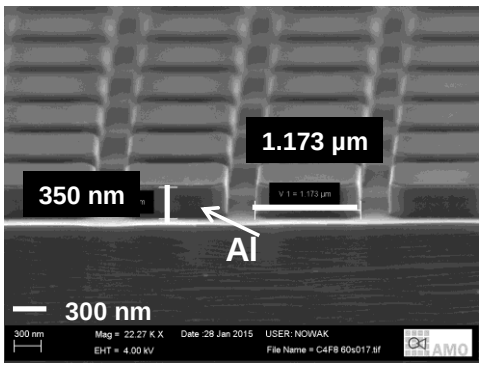


Fig. 6. SEM images of imprinted (a) mr-NIL210 octahedron patterns fabricated via surface conformal imprint lithography (SCIL) and transferred structures into Al using BCl_3 ICP-RIE (b).

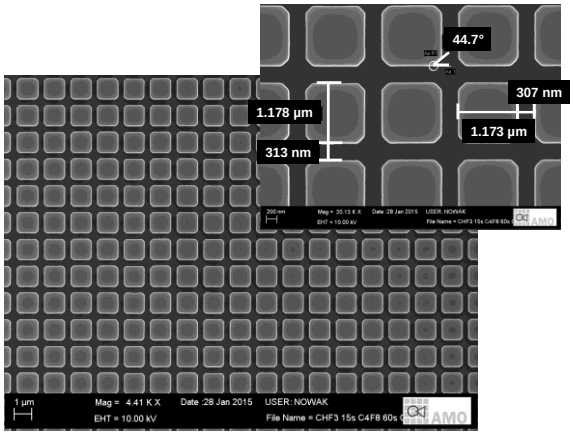


Fig. 7. SEM images of the finally transferred octahedral patterns after RIE process using BCl_3 plasma for aluminum etching demonstrating the excellent lateral pattern transfer accuracy of mr-NIL210.

3. Conclusions

We report on a newly developed photo-curable resist mr-NIL210 with enhanced properties compared to generic NIL resists while being applied in combination with PDMS-based working stamps during soft NIL. We have demonstrated the distinguished film forming properties making mr-NIL210 highly attractive for industrial high volume manufacturing processes. The film stability of mr-NIL210 after spin-coating was demonstrated for a period of 24h without any loss in film homogeneity and without any increase of the edge bead dimension indicating a superior storage capability of already spin-coated wafer cassettes.

The usability of mr-NIL210 in combination with PDMS-based working stamps was demonstrated by a sequentially performed imprint using one single PDMS stamp. After 30 consecutively performed imprints into mr-NIL210 no change in pattern dimension could be observed, rendering the mr-NIL210 as highly suitable for soft NIL applications. Different dimensions of imprinted structures in the range of micrometers as well as nanometers attesting the newly developed resist great replication fidelity during different applied soft NIL technologies.

Preliminary dry etching investigations have resulted in meaningful dry etching selectivity to different substrate materials like silicon, sapphire, or titanium. Further, more detailed etch investigations evidenced, that imprinted structures of mr-NIL210 can be transferred very precisely and effectively in different types of relevant substrate materials like silicon and aluminum, respectively. Thus, mr-NIL210 is superior over generic resist solutions by many means.

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