mr-NIL200 Series: UV-curable NIL Resist Formulation with Self-Priming Properties

Characteristics

The liquid photo-curable NIL resist formulation mr-NIL200 is specifically developed and highly adequate for UV nanoimprint lithography (UV-NIL, Photo-NIL) applying gas-impermeable stamp materials like SiO_2, glass, gas-impermeable polymers like OrmoStamp® or polymer foils like COC, PUA and others. The typical application field of mr-NIL200 is the use as an etch mask in pattern transfer processes.

mr-NIL200 is provided as ready-to-use formulation and can be used for silicon, sapphire, or other substrates materials without the need of any additional adhesion promoter or primer. A customized adjustment of the film thickness can be done on request.

Processing Scheme UV-NIL

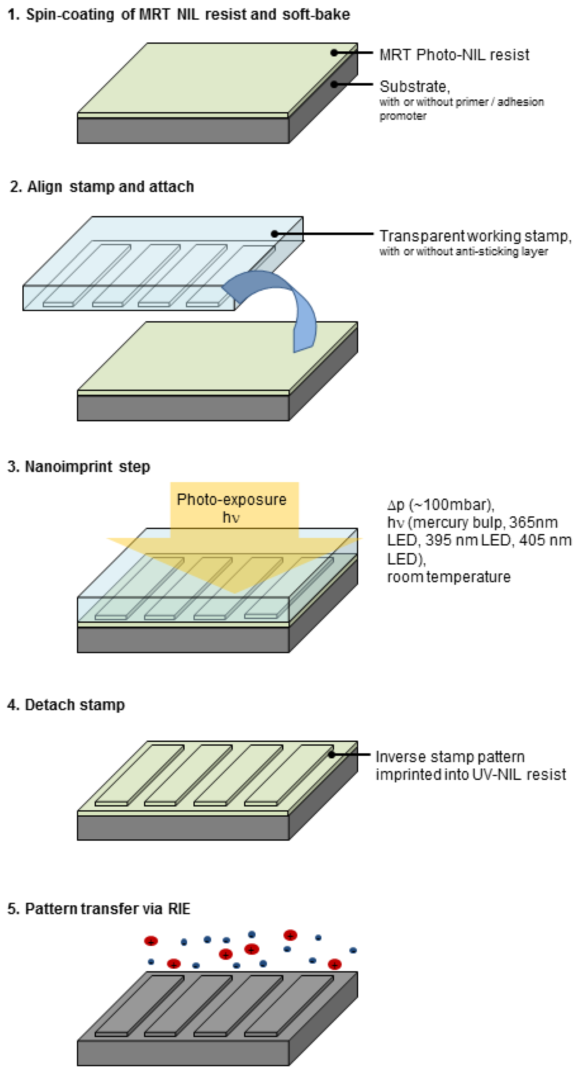

Fig. 1: General process scheme of soft Photo-NIL with photo-curable mr-NIL200.

Processing Details

Resist formulations			**mr-NIL200-100nm**	**mr-NIL200-200nm**	**mr-NIL200-300nm**
Film thickness in nm			**100 ± 15**	**200 ± 20**	**300 ± 20**
Substrate preparation			Spin clean with 2-propanol and dehydrate on a hotplate at 200 °C for 5 min or apply O_2 plasma treatment		
Coating	spin speed	[rpm]	3000		
	time	[s]	30		
	acceleration	[rpm/s]	1000		
Prebake	(hotplate)	[°C]	60		
		[min]	3		
Imprinting parameters					
	Imprint Temperature	[°C]	room temperature		
	Imprint Time	[min]	depending on structure architecture		
	Imprint Pressure	[bar]	100 mbar		
	UV exposure	[mJ/cm^2]	1000 at broadband irradiation		
	Release Temperature	[°C]	room temperature		

Standard Processing Conditions

Best results are accomplished at temperatures of 20–25 °C and a relative humidity of 40–46 %. The specific process parameters depend on substrate material, equipment, and application.

Dilution of mr-NIL200 series

mr-NIL200 formulations can be further diluted to achieve lower film thickness upon spin coating as originally specified. Specific film thickness ranges can be obtained by variation of the diluent/solution mass ratio. Dilution ratios can be provided on request, mixing ratios are given in the attachment of this document.
It is highly recommended to filter the diluted mr-NIL200 formulations again in order to remove particles by unintended contamination. Syringe filters with pore sizes in the range 0.1–1.0 µm can be applied. The recommended diluent is ma-T 1078.
It is strongly recommended that the target film thickness is purchased as ready-to-use formulation directly from *micro resist technology* GmbH. In case of dilution by the user the product quality is no longer guaranteed.

Substrate Preparation

The substrates have to be free of impurities and moisture. Silicon substrates should be spin-cleaned with acetone / 2-propanol, baked at 200 °C for 5 min. and cooled down to room temperature immediately before coating. Alternatively, short oxygen or ozone plasma cleaning is recommended.

Coating

Uniform coatings are obtained by spin coating of the resist formulations. A spin time of at least 30 s is recommended. Extended spin duration time is considered to decrease the film thickness and may improve also the film thickness homogeneity.

Prebake

Spin-coated resist films are annealed on a hotplate at 60 °C for 3 min. This pre-imprint bake is necessary to remove residual solvent that is still in the spin-coated film.

Stamp Preparation

Hard stamps:
Si, Quartz, Ni, etc.: For defect-free imprints and low release forces using silicon, nickel or quartz stamps, it is highly recommended to treat and equip the stamp surface with a release agent. A well-suited release agent for silicon or silicon dioxide is F_{13}-TCS (trichloro-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-silane, CAS number [78560-45-9]), that is commercially available from many suppliers of specialty chemicals.
Hard polymer stamps: mr-NIL200 can also be used in combination with hard polymeric working stamps like the commercially available product OrmoStamp®. Please follow the separate processing guidelines for the stamp preparation with OrmoStamp®.

Soft stamps:
PDMS: mr-NIL200 is not suitable for soft Photo-NIL technology in combination with PDMS stamps.
Other soft stamp materials: mr-NIL200 is a newly developed resist formulation specifically dedicated for a use with hard and gas-impermeable stamp materials. However, a use in combination with other soft stamp materials like PFPE-type or COC-type working stamps is conceivable, but has not yet been comprehensively investigated.

Imprint Conditions

Main factors determining the imprint conditions are the rheological behaviour of the polymer, the mould layout (feature size, density of the patterns etc.), the residual layer thickness to be attained and the imprinting tool. The mr-NIL200 series can be imprinted in any tool suitable for doing thermal nanoimprint lithography. Commercial nanoimprint tools as provided e.g. by EV Group (AUT), SUSS MicroTec (GER), NIL Technology (DEN), Obducat (SWE), or others may be used.
It is recommended to imprint on the lower end of the process window and to choose rather low pressure values. mr-NIL200 performs well because of its optimised flow properties. Very high imprinting pressures are proven to be a source of defects and should be avoided.

Residual polymer layer removal

The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by reactive ion etching (RIE) in order to open the window to the substrate. Oxygen plasma can be used for removal of the residual layer.

Pattern transfer via Reactive Ion Etching (RIE)

mr-NIL200 is usually applied as etch mask for nano-pattern transfer via RIE processes. Exact parameters of the etching process are defined by the nature of the etching tool, etch chamber conditions, plasma gases, gas flow, chamber pressure, platen power, density of structures etc. Hence, the perfect etching condition needs to be developed application wise by the user.

Removal / Stripping

Plasma-based removal: Residue-free removal of processed resist residues is preferably achieved by applying oxygen plasma. Since it only contains organic components, there are no residuals left on the substrate after plasma treatment with pure oxygen.
Wet-chemical stripping: As the cured and processed resists have formed 3D polymer networks during exposure, drastic conditions for wet-chemical removal are necessary for the series.

- Hot piranha etch (H_2SO_4 / H_2O_2) can remove resist residues.
- Solvent treatment in an ultrasonic bath at higher temperature (40–60 °C) for several hours will usually result in a peel off of resist residues. The solvents PGMEA, anisole, NMP-based solvents (e.g. mr-Rem 660) or NMP-free alternatives (e.g. mr-Rem700) can be used.

Storage

We recommend 5–15 °C as standard storage temperature (refrigerator), whereby 18–25 °C is the regular working temperature. Make sure before the use of the resist that the liquid already reached room temperature before opening the bottle to prevent for contamination by humidity. Keep the bottles closed when not in use. Under these conditions a shelf life of 6 months from the date of manufacture is ensured.

Disposal

Dispose of mr-NIL200 formulations as halogen-free solvent.

Environmental and Health Protection

The mr-NIL200 solutions are non-hazardous materials. Nevertheless, they should be handled with same care as all chemicals. Ensure that there is adequate ventilation while processing the materials. Avoid contact with skin and eyes and breathing solvent vapours. Wear suitable protective clothing, safety goggles and gloves.

Attachment

Specifications

Resist formulation	**mr-NIL200-100nm**	**mr-NIL200-200nm**	**mr-NIL200-300nm**
Film thickness [1] [nm]	100 ± 15	200 ± 20	300 ± 25
Appearence, colour	clear, colourless		
Dynamic viscosity 25 °C [mPas]	1.3 ± 0.2	1.4 ± 0.2	1.6 ± 0.2
Refractive index n_D^{25} [2]	1.435 ± 0.002	1.438 ± 0.002	1.441 ± 0.002

[1] Spin-coated at 3000 rpm for 30 s [2] Refractive index of the ready-to-use solution at 589 nm

Physical parameters of the mr-NIL200 resist

mr-NIL200 before UV curing	
Consistency	Liquid polymer precursor
mr-NIL200 after processing (imprinted and UV-cured)	
Glass transition temperature T_g	Fully cross-linked material. No detectable and measurable T_g.
Material classification	Durομeric polymer network

Dilution of mr-NIL200 series

Mass ratio data for dilution [w/w]	
Film thickness @ 3000 rpm	**mr-NIL200-300nm / ma-T 1078**
100 nm	1.0 / 1.50
200 nm	1.0 / 0.39
Film thickness @ 3000 rpm	**mr-NIL200-200nm / ma-T 1078**
100 nm	1.0 / 0.80

Film thickness and spin curves

The thickness data of spin-coated films refer to an open spin-coating system. For film thickness measurements using ellipsometric methods the following Cauchy coefficients can be used: $n_0 = 1{,}496 \pm 0{,}0006$, $n_1 = 68{,}1 \pm 0{,}55\ \text{nm}^2$

Cauchy formula

$$n(\lambda) = n_0 + C_0 \frac{n_1}{\lambda^2} + C_1 \frac{n_2}{\lambda^4},$$

$$C_0 = 10^2, \qquad C_1 = 10^7.$$

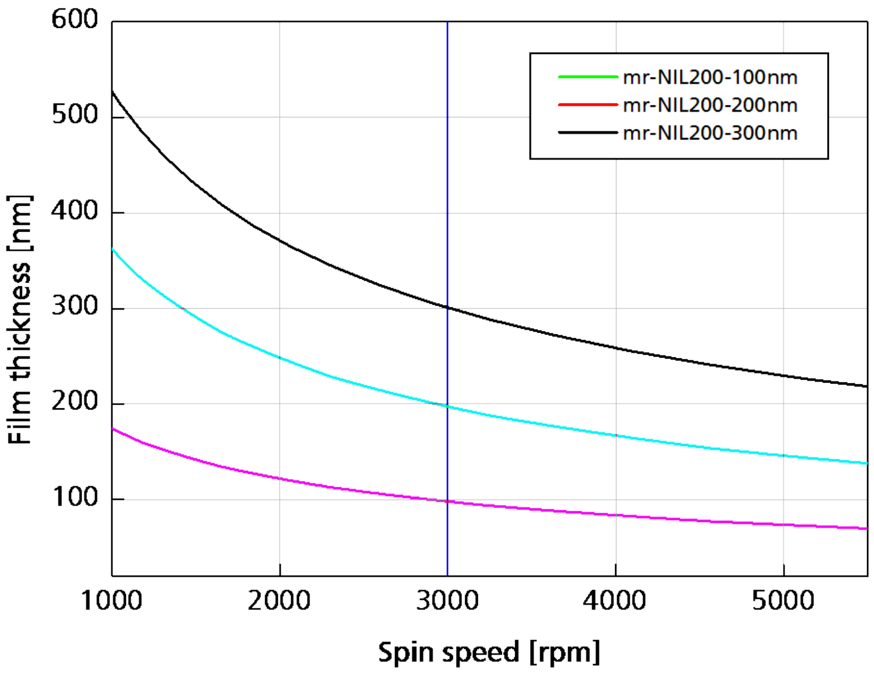

Figure 1. Spin curves of mr-NIL200-100nm, mr-NIL200-200nm and mr-NIL200-300nm, resulting a film thickness of 100, 200 and 300 nm at a spin speed of 3000 rpm, respectively. (30 s spin time, liquid film thickness after spin coating and annealing step).