

Processing Guidelines – OrmoStamp®

OrmoStamp®

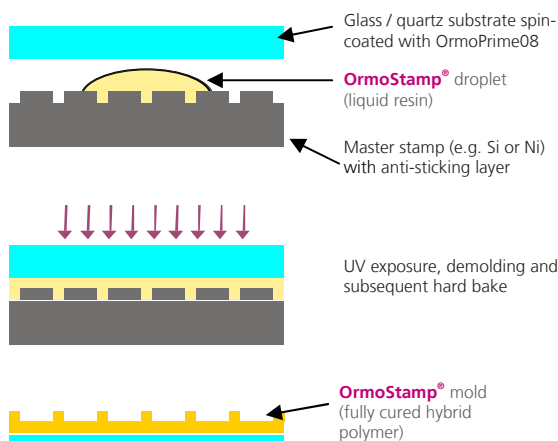
Characteristics

OrmoStamp® is an inorganic-organic hybrid polymer for the easy fabrication of transparent working stamps used in nanoimprint lithography (NIL) as a cost-effective alternative to quartz or electroplated stamps. OrmoStamp® can be applied in thermal NIL and/or UV-based NIL. Stamp copies fabricated using OrmoStamp® hybrid polymer show

- Excellent mechanical properties (combined with sufficient bulk flexibility)
- Ultra-high resolution capabilities down to the sub-10 nm regime
- High transparency for UV and visible light
- High chemical and physical stability (enabling imprint temperatures up to 160 °C)
- Moderate volume shrinkage during cross-linking
- Long stamp lifetime (i.e. mechanical stability and UV transparency)

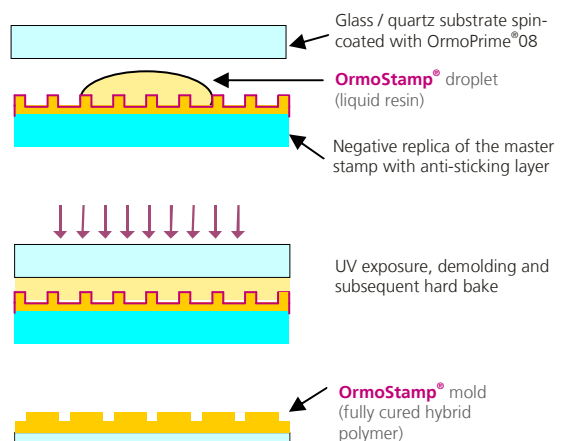
Process Flow

Replication of master stamp



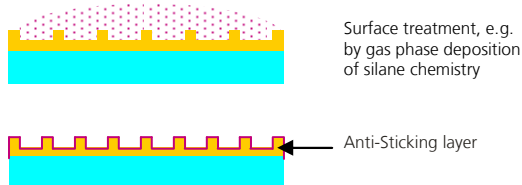
Negative replica of the master stamp

Polarity inversion (optional)



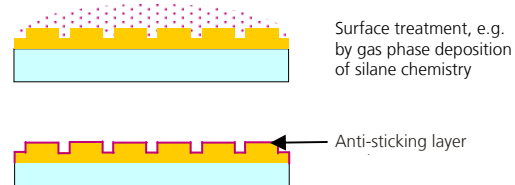
Positive replica of the master stamp

Anti-sticking layer treatment



OrmoStamp® working stamp with anti-sticking layer and negative polarity

Anti-sticking layer treatment



OrmoStamp® working stamp with anti-sticking layer and positive polarity

Fig. 1: Process flow for the manufacture of transparent working stamps by using standard processing equipment. OrmoStamp® is spin-coated or casted on the master original.

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Standard Processing Conditions

Best results are accomplished at temperatures of 20–25 °C and a relative humidity of 40–46 %. **OrmoStamp® has to be processed under yellow light.** The guidelines relate to standard processing on silicon, glass, or silicon dioxide. The specific process parameters depend on substrate, application, and equipment.

Processing Details

The UV-curable resin is a solvent free ready-to-use formulation and can be processed with standard lithography equipment (i.e. spin-coating or casting) prior to UV-initiated crosslinking.

OrmoStamp®		
Film thickness: droplet dispensing		Depends on material quantity applied
spin coating	[µm]	10 ± 1
Substrate preparation		Spin clean with 2-propanol and dehydrate on a hotplate at 200 °C for 5 min or apply O ₂ plasma treatment
Spin coating	spin speed [rpm]	3000
	time [s]	30
	acceleration [rpm/s]	1000
Prebake (hotplate)	[°C]	80
	[min]	2
Exposure dose (365 nm) ^{1,2}	[mJ/cm ²]	1000
Hardbake (hotplate)	[°C]	130
	[min]	10 – 30
Development (OrmoDev) ³	[s]	60 – 180

¹ Flood exposure after development is recommended when lower doses were used for patterning and high mechanical and thermal stability is required. Higher exposure dose will also improve the adhesion to the substrate.

² Broadband exposure, intensity measured at $\lambda = 365$ nm

³ Immersion development, time may vary depending on feature size

Master Stamp Preparation

In order to avoid any damage to the master stamp, the use of a suitable anti-sticking layer is recommended. The most common release agent for silicon or silicon dioxide is "F13-TCS" (1H,1H,2H,2H-perfluorooctyl-trichlorosilane, CAS number [78560-45-9], available from common suppliers of specialty chemicals).

Substrate Preparation

In order to achieve an optimized adhesion of OrmoStamp® to silicon, glass or quartz substrates, it is highly advisable to use an adhesion promoter such as OrmoPrime®08. For processing information please see the OrmoPrime®08 processing guidelines.

In any case, the substrate has to be free of impurities and moisture prior to OrmoStamp® coating. It should be spin-cleaned with acetone/ 2-propanol, baked at 200 °C for 5 min and cooled to room temperature immediately before coating. Alternatively, short oxygen or ozone plasma cleaning is recommended. Pre-cleaning with a gentle etching agent (e.g. acetic acid) will also improve the adhesion to glass.

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Coating Option: Droplet Dispensing

For the easy manufacture of working stamp copies, it is recommended to use casting rather than spin coating. A cohesive and bubble-free OrmoStamp® droplet should be dispensed directly on the master stamp (properly coated with an anti-sticking layer) using a pipette. Note, that the final height of OrmoStamp® layer is determined by the dispensed amount of material. Therefore, cast a defined quantity onto the master and avoid excessive use of OrmoStamp® to allow proper handling, processing and demolding. The following table helps finding appropriate coating parameters for OrmoStamp® layers with thickness of 150–170 µm. The exact quantities may differ depending on master stamp structures.

Master stamp size	OrmoStamp® quantity [g]
25 x 25 mm ²	0.045
2" wafer	0.20
4" wafer	1.0 – 1.2
5" wafer	2.4
6" wafer	3.5

Coating Option: Spin Coating

If necessary, the liquid OrmoStamp® resin can be spin-coated on the (transparent) substrate using standard processing equipment. The respective spin curve can be found in the attachment, which refers to an open spin-coating system. A prebake step for 2 min at 80 °C step is optional, since OrmoStamp® is a solvent free material. The thermal treatment increases the film homogeneity and the adhesion to the substrate. Note, that OrmoStamp® remains still liquid after the prebake.

Replication

The (transparent) substrate coated with an adhesion promoter is carefully placed onto the liquid OrmoStamp® droplet to avoid air inclusions which will lead to inaccurate replication. In some cases, the stack can be gently pressed to facilitate the OrmoStamp® to spread to a film while the air is squeezed out of the closing gap between substrate and master. Since the resistance of flow is increasing when the gap is continuously closing, the spreading of liquid OrmoStamp® requires 5–15 min. If the procedure is properly followed, OrmoStamp® will completely fill the gap between stamp and substrate due to capillary forces.

Exposure and Demolding

OrmoStamp® is sensitive for UV broadband, i-line (365 nm), or h-line exposure (405 nm). UV curing leads to volume shrinkage in the range of 4–6 %. Applying a UV overdose during curing does not affect OrmoStamp®'s properties. Keep the substrate-mold stack always horizontal until the resin is fully cured. In order to allow the easy demolding of master stamp and UV-cured replica, the OrmoStamp® formulation contains fluorine based additives for decreased release forces. We recommend an additional UV-flood exposure after demolding, when the dose applied prior to demolding was lower than 1000 mJ/cm².

Development

This process step is optional and only necessary when uncured material has to be removed. Ready-to-use developer OrmoDev is recommended in this case. The temperature of the developer should be 20–25 °C. Thoroughly rinse with 2-propanol and gently blow-dry with nitrogen.

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Hard Bake

For increased thermal and environmental stability, a hard bake is required. It is advisable to ramp the temperature slowly during heating and cooling period, since abrupt changes in temperature might lead to delamination of OrmoStamp®. The hard bake can be accomplished on a hot plate at 130 °C for at least 30 minutes.

Anti-sticking Layer Treatment

The working stamp fabrication is finalized by applying a fluorosilane based anti-sticking layer (e.g. 1H,1H,2H,2H perfluorooctyl-trichlorsilane, CAS [78560-45-9]) to the OrmoStamp® hybrid polymer, which has to be treated with a gentle O₂ plasma treatment prior to anti-sticking layer treatment. This removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding). However, only a short and gentle oxygen process is recommended to avoid formation of porous silicon dioxide! After deposition, excessive silane accumulations can be removed using an ultrasonic bath supported by acetone and IPA cleaning.

Removal

As OrmoStamp® forms a three-dimensional polymer network during curing, drastic conditions for removal are necessary. The solvent PGMEA or NMP-based solvents in an ultrasonic bath at higher temperature (40-60 °C) for several hours will usually result in a peel off. Hot piranha etch is also suitable. Alternatively dry etching with O₂/CHF₃ plasma can be used to remove the cured hybrid polymer.

Do not use pure oxygen plasma! Porous SiO₂ will be formed.

Storage

We recommend 5–15 °C as standard storage temperature (refrigerator), whereby 18–25 °C is the regular working temperature. Under these conditions a shelf life of 6 months from the date of manufacture is ensured. Storage conditions deviating from these recommendations can lead to pre-aging (e.g. higher viscosity or insufficient curing upon UV exposure after room temperature storage for several weeks). OrmoStamp® and unprocessed material have to be stored under yellow light. Keep the bottle closed when not in use.

Disposal

Unexposed material: dispose of as halogen-free solvent.

Exposed material: dispose of as solid chemical waste.

Environmental and Health Protection

OrmoStamp® is a non-hazardous good. However, it should be handled with same care as all chemicals. Ensure that there is adequate ventilation while processing the material. Avoid contact of OrmoStamp® with skin and eyes and breathing solvent vapours. Wear suitable protective clothing, safety goggles and gloves.

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Processing Guidelines – OrmoStamp®

Attachment

OrmoStamp® Specifications

Liquid OrmoStamp® resin (uncured)		
Viscosity @ 25 °C (solvent free)	[Pa s]	0.5 ± 0.2
Density	[g cm ⁻³]	1.14 ± 0.01
Refractive index n _D ²⁵		1.485 ± 0.002
Spectral sensitivity (UV curing)	[nm]	300 – 410
Filtration level	[µm]	0.8

Physical Parameters of Processed OrmoStamp® Hybrid Polymer

Cured OrmoStamp® hybrid polymer (UV-exposed and hard baked) ¹		
Thermal behaviour		Duromeric
Volume shrinkage ²	[%]	4–6
Optical dispersion		See Fig. 2
CTE (20 – 100 °C)	[ppm K ⁻¹]	105
Modulus of elasticity	[MPa]	650
Hardness (by indentation)	[MPa]	36 ± 1

¹ Sample processing: (1) UV dose 1000 mJ/cm², (2) post exposure bake: hotplate 10 min @ 130 °C

² Exact degree of shrinkage depends on specific processing conditions and pattern size

Film Thickness and Spin Curve

The film thickness was measured after UV exposure. Standard hard bake process was applied to the OrmoStamp® layer. The data refer to an open spin-coating system.

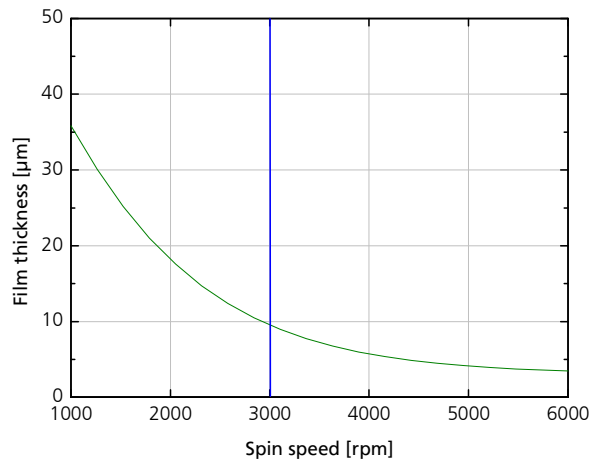


Fig. 1: Spin curve of OrmoStamp®, 30 s spin time (1000 mJ/cm² UV dose and hard bake @ 130 °C).

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Optical Properties

The high UV transparency of OrmoStamp® is preserved upon thermal treatment and therefore allows OrmoStamp® to be used in both, UV-based and thermal replication processes.

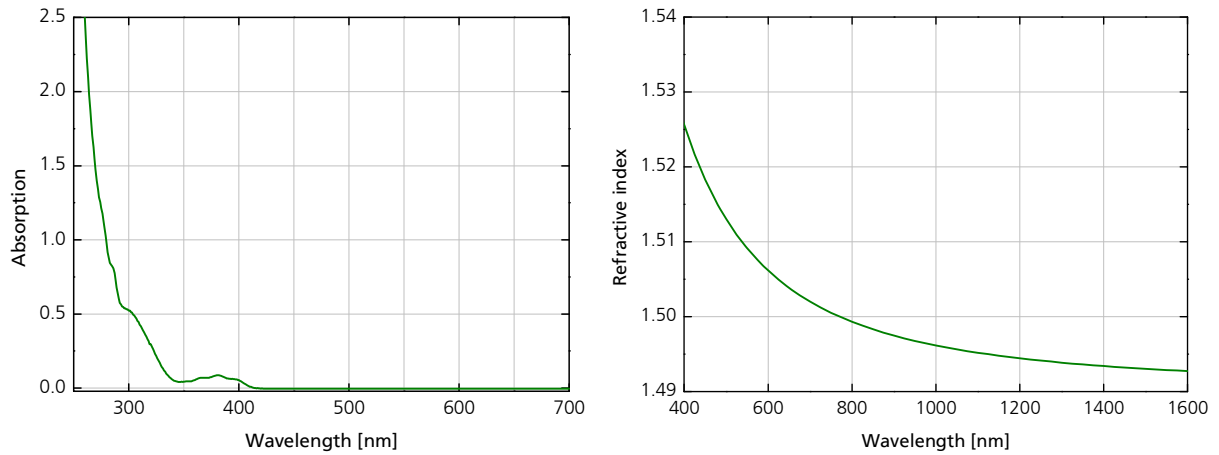


Fig. 2: Wavelength dependent absorption of a 200 µm thick OrmoStamp® layer on quartz substrate and the refractive index. The OrmoStamp® film was UV exposed and hard baked according to standard processing conditions.

OrmoStamp®: DE 30 210 075 435; IR 1 092 621 ; TW 100030629 (application)
OrmoPrime®: DE 30 210 075 436

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