New material solutions for industrial LED production

Marko Vogler, Manuel Thesen, Anja Voigt, Arne Schleunitz

*micro resist technology GmbH*
Köpenicker Str. 325
12555 Berlin, Germany

*Ahead Optoelectronics, Inc.*
5F, No. 66, Jian-San Road
Chungho, New Taipei City 235 Taiwan
Outline

• Company Introduction and Products
• Innovative material solutions for industrial LED production
  1. Patterned sapphire substrates by nanoimprint lithography
  2. Photonic crystal for HB-LEDS patterns by nanoimprint lithography
  3. Alternative LED fabrication concept: Nanowire approach
  4. Photoresists for lift-off applications, single layer processes
  5. Potential Alternative Materials for LED packaging: Hybrid polymers
• Summary
micro resist technology GmbH – Company Facts

Producer, developer & supplier of innovative resists, polymers, photopolymers, ancillaries for use in MEMS applications, semiconductor industry, micro and nanotechnology and optoelectronics

- **Established:**
  1993 as a chemical company

- **Employees:** 52 (2015)

- **Facility:**
  Since 2011 new facility with 2.500 m² incl. production, clean room, office space (MRT total: 3.450 m² facility)

- **Certifications:**
  DIN EN ISO 9001:2009
  DIN EN ISO 14001
# micro resist technology GmbH - Product Groups

## Negative Photoresists
- UV resists for single layer lift-off
  - ma-N 400
  - ma-N 1400
- DUV/ e-beam resists
  - ma-N 2400
  - mr-EBL 6000
- Direct Laser Writing
  - mr-DWL @ 405 nm
- Waveguide application
  - EpoCore / EpoClad

## Positive Photoresists
- Standard UV-resists
  - ma-P 1200
- High viscosity UV-resists
  - ma-P 1275/
  - ma-P 1275HV
- Greyscale UV-resists
  - ma-P 1275G

## NIL Materials
- Thermal NIL
  - mr-I 7000R/ 8000R
  - mr-I T85
  - mr-I 9000M
  - SIPOL
- Thermal / UV NIL
  - mr-NIL 6000E
- UV-based NIL
  - mr-NIL210
  - mr-UVCur series
  - mr-XNIL series

## Hybrid Polymers
- Inorganic-organic hybrid polymers
- Optical application
  - OrmoComp®
  - OrmoClear®FX
  - InkOrmo
- Waveguide application
  - OrmoCore
  - OrmoClad
- Transparent stamps
  - OrmoStamp®

## Distribution in Europe for:
- Dow Electronic Materials, MicroChem Corp. (SU 8/2000/3000, PMGI, PMMA),
- DuPont (Dry film), ShinEtsu (Photo-curable PDMS)
micro resist technology GmbH – business fields, markets

**Energy & Lighting Technology**
- High brightness LED
- Nanotextured solar cells
- OLED devices
- Opto-Electronics

**Consumer Electronics Display Technology**
- Micro lenses
- Sensors & Actuators
- Backlighting devices
- Mass storage devices

**Health Care Life-Sciences**
- Microfluidics & Microarrays
- Waveguides & X-ray lenses
- Surface functionalization (Biomimetics)

**Security Features**
- Holographic images protecting products and documents

**Manufacturing**
- Technology enabling materials
micro resist technology GmbH – global exports

Joint booth: K0525
5 application examples along the LED production chain:

1. Patterned sapphire substrates by nanoimprint lithography
2. Photonic crystal for HB-LEDs patterns by nanoimprint lithography
3. Alternative LED fabrication concept: Nanowire approach
4. Photoresists for lift-off applications, single layer processes
5. Potential alternative materials for LED packaging: Hybrid polymers
Patterned Sapphire Substrates (PSS) for HB-LEDs by nanoimprint lithography (NIL)

- NIL as cost-efficient alternative to stepper lithography
- Nanoimprint Resists by *micro resist technology*
  - mr-NIL 6000E series
  - mr-NIL210 series (PDMS compatibility)
## What is Nanoimprint Lithography?

### NIL process scheme

<table>
<thead>
<tr>
<th>Process step</th>
<th>Thermal-NIL</th>
<th>UV-NIL</th>
<th>Combined Thermal and Photo-NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>Resist deposition (spin coating, inkjet, etc.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>②</td>
<td>Solid film</td>
<td>Liquid film</td>
<td>Solid film</td>
</tr>
<tr>
<td>③</td>
<td>T &gt; T&lt;sub&gt;g&lt;/sub&gt; = T&lt;sub&gt;imprint&lt;/sub&gt;</td>
<td></td>
<td>T &gt; T&lt;sub&gt;g&lt;/sub&gt; = T&lt;sub&gt;imprint&lt;/sub&gt;</td>
</tr>
<tr>
<td>④</td>
<td>Δp</td>
<td>(photo-curing @ RT)</td>
<td>Δp</td>
</tr>
<tr>
<td>⑤</td>
<td>T &lt; T&lt;sub&gt;g&lt;/sub&gt;</td>
<td></td>
<td>(photo-curing)</td>
</tr>
<tr>
<td>⑥</td>
<td>Stamp release</td>
<td>Stamp release</td>
<td>Stamp release @ T&lt;sub&gt;imprint&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Soft UV-NIL technology

Standard Plate-to-Plate NIL Method

- Rigid substrates
- Rigid stamps

Stamp materials in use:
Si, SiO₂, Ni, „hard“ polymers (e.g. COC, OrmoStamp®)

Soft-NIL Technology

- Rigid, flexible or arbitrary shaped substrates
- Flexible stamps

Stamp materials in use:
Elastomers like PDMS, PFPE

Easy processing, low defect rate → growing industrial interest for HVM
### State of the Art

**Sylgard 184 PDMS**
- Short admixed pot life time of 1.5 h
- Comparatively low Young’s Modulus

**Generic resist formulations**
- Stamp contamination by resist diffusion into PDMS over time
- Reduced stamp lifetime → typical imprint cycles ~25 with same PDMS stamp
- Limited potential for adjustment and development

### Our Material Proposition

**UV-PDMS KER-4690**
- Pot life after mixing of several hours (> 24h) → longer time window for processing
- Two times higher Young’s Modulus

**mr-NIL210 series**
- Negligible diffusion of resist components into PDMS
- Strongly enhanced stamp lifetime → 50 imprints verified for X-PDMS and Sylgard 184, 30 cycles demonstrated with KER-4690
- Formulation based on modularity → customized tailoring feasible
Soft UV-NIL – Evaluation of long-term PDMS compatibility

Can components of mr-NIL210 permeate into PDMS stamp material?

Highly relevant for long-term PDMS-compatibility (high volume production)

Empirically evaluated by an extended contact time period between uncured mr-NIL210 and PDMS-stamp

In case of (slow) permeation

Imprint defects

In case of (fast) permeation

Negligible permeation

No imprint defects
Patterned Sapphire Substrates – Pattern Transfer by Dry Etching

mr-NIL210 series

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working stamp</td>
<td>UV-PDMS KER-4690</td>
</tr>
<tr>
<td>Area</td>
<td>10 x 10 cm²</td>
</tr>
<tr>
<td>Substrate</td>
<td>4 inch sapphire w/o Primer</td>
</tr>
<tr>
<td>Imprint</td>
<td>1000 mJ cm⁻² Hg bulb (365 nm) radiation, capillary force imprinting</td>
</tr>
<tr>
<td>Resist</td>
<td>mr-NIL210 series</td>
</tr>
<tr>
<td>Initial layer thickness</td>
<td>500 nm, minimized residual layer thickness</td>
</tr>
</tbody>
</table>

Verification of PSS fabrication by chlorine based dry etching using mr-NIL210 series

→ Selectivity 0.87
Photonic Crystals for HB-LEDs by nanoimprint lithography

- High aspect ratio patterns required (>3:1) in III-V materials
- Nanoimprint Resists for GaN patterning:
  - Etch-stable mr-I 8000R
  - SIPOL bilayer approach
Realization of High-brightness LEDs by Nanoimprint

Photonic crystals → Selective Area Photonic Crystals (SPC) via NIL using mr-I 8000R (thermal NIL)

No photonic crystal (NPC)

Full area photonic crystal (FPC)

Selective area photonic crystal (SPC)

78% output power enhancement using selective area photonic crystal (SPC)

**SIPOL** for high-aspect-ratio pattern fabrication

- Bilayer approach using transfer layer
- For patterned sapphire or GaN substrates
- Contains Silicon → **high dry etch resistance**

**SIPOL imprint and dry etch process**

- **SIPOL**
  - Transfer layer UL1
  - GaN / sapphire

- Low aspect ratio imprint
  - T-NIL
  - GaN / sapphire

- Etching of residual layer
  - Cl, F RIE
  - GaN / sapphire
  - O₂ RIE

- Formation of SiO₂ and relief amplification
  - Cl, F RIE
  - GaN / sapphire

First results: AR10 L&S in Si (Bosch process)

**M Meserschmidt et al. Microelectron Eng 98 2012 107**
Innovative material solutions 3

LED production chain

Alternative LED fabrication concept: Nanowire approach
- True white light LED chip without the need of an additional phosphor
- Nanowire fabrication by means of **nanoimprint lithography (NIL)**
  - Imprinting nanoholes and nanopattern transfer for controlled nanowire growing
  - Various nanoimprint resists available (mr-I 9000M)
LED production chain

Photoresists for single layer lift-off applications

- Fabrication of electrical contacts (Ag) and microelectronic finishing
- UV lithography, pattern transfer with PVD, and lift-off
- Negative photoresists:
  - ma-N 400 series
  - ma-N 1400 series
Negative Resists for UV lithography

ma-N 400 & ma-N 1400 series: conventional pattern transfer and single layer lift-off processes

- Excellent suitable for physical vapour deposition (PVD) and lift-off exhibiting tunable pattern profile
- High dry and wet etch resistance
- Good - excellent thermal stability of the resist patterns
- Suitable for broadband and i-line exposure
- Aqueous alkaline development
- Easy removal

Applications:
- Microelectronics and micro system technology
- Mask for lift-off processes
- Etch mask for semiconductors and metals
Negative Resists for UV lithography

**ma-N 400 & ma-N 1400 series: generation of undercut patterns**

**ma-N 400**, 2 µm thick, develop with ma-D 332/S

- **Time** → undercut
  - 90 s → 0 µm
  - 100 s → 0.5 µm
  - 140 s → 1.5 µm

**ma-N 1400**, 2 µm thick, develop with ma-D 533/S

- **Time** → undercut
  - 65 s → 0.6 µm
  - 80 s → 0.8 µm
  - 120 s → 2.1 µm

**Differences**

- Available film thicknesses
  - up to 7 µm ma-N 1400
  - up to 14 µm ma-N 400

- Sensitivity

- Thermal stability:
  - up to 160 °C ma-N 1400
  - up to 110 °C ma-N 400

- Shape of undercut
Potential Alternative Materials for LED Packaging: Hybrid polymers

- Hybrid polymers originally developed for micro-optical applications
- Excellent thermal stability and climate stability
- Alternative polymer matrix for the phosphors for white LEDs
  - **OrmoClear types**
UV-curable Inorganic-organic Hybrid Polymers

**Inorganic-organic Hybrid Polymers based on ORMOCER® technology**

- Optical (glass-like) polymers for micro-optical applications
- Multifunctional lithography material with negative resist behavior
- Application by spin-coating, casting, dispensing, ink-jetting,...
- LED- and Laser-based exposure

ORMOCER®s for micro-optics licensed by the Fraunhofergesellschaft zur Förderung der Angewandten Forschung in Deutschland e.V.

**Unique features**

- High thermal stability
- Excellent transparency
- Excellent mechanical properties
- High chemical and physical stability
- Excellent replication fidelity
Advanced Stability Features of Hybrid Polymers

General thermal stability of hybrid polymer products

- Thermal cycling test passed (layers on glass): 40x –40 °C to 85 °C
- Long term test passed: 3 days at 85°C and 85 % rel. humidity
- Slow decomposition only >300°C (TGA/DTG):

![Graph showing thermal stability data](image-url)
Advanced Stability Features of Hybrid Polymers

Tests regarding optical properties
– *Sunlight* and *thermal cycling reliability test* (1.5 µm OrmoComp®)
  → excellent optical properties preserved
– *SMT solder bump reflow test*: 3 x 6 min @ 260 °C
  → no yellowing observed
– *UV stability tests* passed: 300 h UV exposure at 60 °C
  → no influence on optical properties

Stability tests important for LED packaging:
– 440 nm exposure at 120°C, dose 2 W/cm², 7 weeks (1176 h)
  → no yellowing for OrmoClear
  → Polymer layers still optically clear
– Further tests under investigation

→ Material proposition: hybrid polymer OrmoClear as polymer matrix for the phosphors for white LEDs
### micro resist technology GmbH – Summary

#### Negative Photoresists
- UV resists for single layer lift-off
  - ma-N 400
  - ma-N 1400
- DUV/ e-beam resists
  - ma-N 2400
  - mr-EBL 6000
- Direct Laser Writing
  - mr-DWL @ 405 nm
- Waveguide application
  - EpoCore / EpoClad

#### Positive Photoresists
- Standard UV-resists
  - ma-P 1200
- High viscosity UV-resists
  - ma-P 1275/
  - ma-P 1275HV
- Greyscale UV-resists
  - ma-P 1275G

#### NIL Materials
- Thermal NIL
  - mr-I 7000R/ 8000R
  - mr-I T85
  - mr-I 9000M
  - SIPOL
- Thermal / UV NIL
  - mr-NIL 6000E
- UV-based NIL
  - mr-NIL210
  - mr-UVCur series
  - mr-XNIL series

#### Hybrid Polymers
- Inorganic-organic hybrid polymers
  - Optical application
    - OrmoComp®
    - OrmoClear®FX
    - InkOrmo
  - Waveguide application
    - OrmoCore
    - OrmoClad
  - Transparent stamps
    - OrmoStamp®

#### Key strength of MRT: Our products can be tailored according to your industrial requirements

#### Our mission is to support emerging nano(fabrication) technologies with tailor-made material innovations
Thank you for your attention!

Come to our booth K0525!

Discuss with us on the **Sapphire Networking Reception** (Thursday 12:00-13:30)!

---

Dr. Marko Vogler  
Chemist  
Business Unit Manager  
Nanoimprint Materials and Hybridpolymers

Köpenicker Str. 325  
12555 Berlin - Germany  
www.microresist.com  
Tel.: +49 30 641670 179  
Fax: +49 30 641670 200  
E-Mail: m.vogler@microresist.de