Advanced Polymers and Resists –
A Key to the Development of Nanoimprint Lithography

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In thermal nanoimprint lithography (NIL), nanometre scale features of a stamp are embossed into a thin polymer layer, which has been heated above its glass transition temperature ($T_g$). In the development of NIL polymer materials have been playing a key role. Process parameters such as imprint temperature, time and pressure depend on the thermomechanical properties of the polymers. High etch resistance is important for transferring nanometre scale imprinted patterns into a substrate.

A survey on polymer systems specifically designed for NIL is given. Thermoplastic methacrylate-based homopolymers and copolymers have been prepared differing in their chemical composition and molecular weights, thermal and flow properties and exhibiting excellent plasma etch resistance.

Curing polymers enable nanoimprinting at moderate temperatures. Macromolecular networks are formed by thermal or photochemical crosslinking. In the first case crosslinking occurs during imprinting, in the second one, imprinting and network formation can be conducted in separate steps. The thermal properties of curing polymers can be controlled by the imprint conditions.

Keywords: nanoimprint lithography, polymers, thermoplastics, curing polymers, low imprint temperature

1. Introduction

Driven by the steadily increasing scale of integration in microelectronics and the as well increasing costs for creating ever-smaller patterns, researchers and technologists have been looking for alternatives to the conventional radiation-based lithographic technologies, which are suited for mass production. One promising approach is thermal nanoimprint lithography (NIL) proposed in 1996 as a high-throughput, low-cost non-traditional technology, which enables creating patterns with feature sizes down to 10 nanometres and below [1]. Much effort has been made in various groups all over the world since then to explore the potential of NIL and to address the critical issues inherent to this new technology. In December 2003, NIL was included in the International Technology Roadmap for Semiconductors (ITRS) as a next-generation lithography candidate to be employed at the 32 nm node recognizing the great potential of NIL for microelectronics. Moreover there are a number of applications in areas outside IC manufacturing, e.g. in integrated optics, micro- and nanofluidics and nanobiology.

The progress and performance of NIL is closely linked with the availability of resists or polymers, which meet all the specific requirements of this technology. Polymers are needed not only working as classical resists to be removed after the pattern transfer. For other applications they also have to serve as permanent materials. Mechanical properties, especially appropriate flow behaviour, play a key role. Depending on the specific application further properties may become important. It is necessary to design polymers specifically meeting both general requirements of the NIL process and of the specific application. micro resist technology GmbH started designing polymers for NIL in 1998. A review and the current status on polymers for NIL are given in this contribution.

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2. NIL process

NIL is a hot embossing process. A mould or stamp is pressed into a thin polymer layer, which was heated above its glass transition temperature ($T_g$). Polymer and stamp are cooled after a specific hold time to a temperature below $T_g$ of the polymer, and the stamp is released. The remaining residual resist layer in the compressed areas is finally removed by anisotropic oxygen plasma etching to open the windows to the substrate (Fig. 1).

![NIL process diagram](image)

Fig. 1. NIL process

3. Mechanical properties of polymers

In the imprint process a thickness contrast is created by deformation of the polymer film. Mechanical properties of the polymers and their temperature dependence govern the patterning condi-

![Storage modulus of PMMA graph](image)

Fig. 2. Storage modulus of PMMA

The curve is characterized by three characteristic transitions: the temperature ranges of a subtransition $T_s$, the glass transition $T_g$ and the flow transition $T_f$.

The mechanical behaviour of a polymer reflected by its Young's or shear modulus is

<table>
<thead>
<tr>
<th>Glassy state</th>
<th>Rubber elastic state</th>
<th>Plastic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_s$</td>
<td>$T_g$</td>
<td>$T_f$</td>
</tr>
<tr>
<td>Hard elastic, brittle</td>
<td>Hard elastic, rigid, leathery</td>
<td>Rubber elastic</td>
</tr>
<tr>
<td>$E_h \sim 3000 \text{ N/mm}^2$</td>
<td>$E_h \sim 1000 \text{ N/mm}^2$</td>
<td>$E_h \sim 1 \text{ N/mm}^2$</td>
</tr>
<tr>
<td>Molecular conformation completely fixed</td>
<td>Molecular conformation largely fixed</td>
<td>Entanglements and physical junction zones prevent movement of entire macromolecules</td>
</tr>
<tr>
<td>Occasional change of molecular positions of side groups and chain segments</td>
<td>Entropy elastic change of molecular position of chain segments</td>
<td>No restricted rotation around single bonds</td>
</tr>
<tr>
<td>Effect of stress: energy elastic distortion</td>
<td>Effect of stress: entropy elastic distortion</td>
<td>Whole macromolecules change their position, pass each other</td>
</tr>
<tr>
<td>Imprinting is possible, but: memory effect</td>
<td>Temperature range for imprinting</td>
<td>Plastic flow</td>
</tr>
</tbody>
</table>

$^1$ Young's modulus
closely related to the molecular mobility of the macromolecules (Table 1). Plastic flow under moderate pressure occurs at temperatures above the flow transition temperature 50 - 80 K above $T_g$ of the polymers. They exhibit sufficiently low viscosity at these temperatures, which is required for a fast imprint process and hence, this is the temperature range, where thermoplastic polymers are usually imprinted.

4. Thermoplastics for NIL

General requirements to polymers for NIL are

- High quality amorphous films
- Good adhesion to the substrate
- High thickness uniformity
- Low viscosity during imprinting
- High pattern transfer fidelity
- No adhesion to the mould
- Sufficient thermal stability in subsequent processes, e.g. RIE, lift-off
- High plasma etch resistance (allows smaller film thickness, aspect ratio and feature size)
- Soluble in non-toxic solvents
- Deposition by spin-coating

Many investigations in NIL were carried out with PMMA. It is well known as an electron-beam resist and much published data is available on this polymer in the literature. PMMA meets most of the demands above. Different from PMMA types with high molecular weights of e.g. 950k, which are used in electron-beam lithography, PMMA for NIL is preferred with molecular weights of 35 – 75 k because of the lower viscosity of these polymers. $T_g$ of PMMA is about 105 °C. Imprint temperatures of 170 - 200 °C are usually applied.

PMMA exhibits low plasma etch resistance, due to its aliphatic character. Its etch resistance is unsatisfactory, when the imprinted patterns shall serve as an etch mask. Alternatives to PMMA were proposed to overcome these limitations. Methacrylate-based polymers and copolymers containing aromatic components were synthesized [2] and are commercially available with $T_g$ values of 60 °C and 115 °C, respectively (mr-I 7000 and mr-I 8000 of micro resist technology GmbH) as well as polymers with customized $T_g$. There are a number of factors having an impact on the processing conditions of NIL, especially

- Polymer
- Mould layout (e.g. feature size, density of the patterns)
- Material of the mould
- Residual layer thickness

- Imprinting tool

That is why the polymer supplier can only give some general processing guidelines. The imprint temperature should be at least 60 K above $T_g$. The release of the mould can be carried out at temperatures not higher than 5 K above $T_g$, to avoid sticking of the polymer to the mould. 50 bar imprint pressure are a good starting point for elaborating a process. Imprint times are reported ranging from below 1 min to several minutes. Fig. 3 shows a possible imprint process scheme of a methacrylate polymer with $T_g$ 60 °C.

![Fig. 3. Imprint process for methacrylate polymer with $T_g$ 60 °C (film thickness 300 nm, (passive) air cooling)](image)

The etch rates of the thermoplastics in a SiO$_2$ etch process are given in Table 2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Etch rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (for comparison)</td>
<td>190</td>
</tr>
<tr>
<td>PMMA</td>
<td>210</td>
</tr>
<tr>
<td>mr-I 7000</td>
<td>100</td>
</tr>
<tr>
<td>mr-I 8000</td>
<td>100</td>
</tr>
</tbody>
</table>

Test patterns in mr-I 7000 are shown in Fig. 4.

![Fig. 4. Test patterns of mr-I 7000 (film thickness 230 nm, 200 nm lines & trenches)](image)

5. Curing polymers

The glass transition in thermoplastic polymers is a reversible process. Therefore imprinted patterns begin to flow and distort, when their temperature approaches $T_g$ of the polymer (Fig. 5).
Fig. 5. 400 nm lines and trenches of a thermoplastic with \( T_g \) 40 °C, immediately after imprinting (left) and the same patterns after heating the imprint to 60 °C for 5 min (right).

Higher deformation resistance is attained, when higher \( T_g \) polymers are used for imprinting. This would require a correspondingly higher imprint temperature entailing a number of drawbacks, among others long processing time (heating and cooling), stress (different coefficients of thermal expansion), and the risk of polymer degradation. Thermally sensitive applications would not be possible under these conditions.

Curing polymers (special precursors of cross-linked polymers, prepolymer) offer the possibility to combine both a comparably low imprint temperature and high thermal stability of the imprinted patterns. The prepolymer are soluble, low molecular weight polymer products, which carry reactive functional groups capable of further polymerizing. Prepolymer solutions can be applied like those of common thermoplastic polymers. On account of the low molecular weight and low \( T_g \) of the prepolymer imprints temperatures around 100 °C can be applied in some cases. The increase in thermal stability of the polymers is based on a cross-linking reaction of the macromolecules. There are two strategies due to the polymerization mechanism of the polymers. Thermally curing and photochemically curing polymers have been developed for NIL [2, 3].

5.1 Thermally curing polymers

In thermally curing polymers, the cross-linking polymerization occurs at elevated temperatures during imprinting. Allyl prepolymer have been synthesized as model compounds for implementing this concept. Physical data of the prepolymer is given in Table 3.

<table>
<thead>
<tr>
<th>Physical properties of allyl prepolymer</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>Molecular weight ( M_w )</td>
<td>95,000</td>
</tr>
<tr>
<td>Density</td>
<td>1.3 g/cm³</td>
</tr>
<tr>
<td>Glass transition temperature ( T_g )</td>
<td>65 °C</td>
</tr>
</tbody>
</table>

There is an interrelationship between imprint time, temperature and degree of cross-linking. The curing rate increases with increased imprint temperature and process duration and can be controlled this way. At the same time \( T_g \) of the polymer and consequently the thermal stability of the polymer increases with the curing progress. The thermal stability of imprinted patterns was determined by annealing wafers with imprinted patterns on a hotplate. The resulting heat distortion was determined as decrease in the pattern height \( \Delta h \) using an atomic force microscope AFM. In Fig. 6 the pattern distortion of 200 nm lines is shown as a function of the imprint temperature.

![Graph showing thermal stability of imprinted prepolymer patterns as a function of imprint temperature](image_url)

The curing reaction (increase in \( T_g \)) starts at temperatures > 140 °C in this case. When this temperature is not applied during the imprinting, the prepolymer behaves like a thermoplastic. As an important conclusion from this graph, the temperature of stamp release has to be chosen in the grey area, where sticking of the polymer to the stamp is minimized.

Thermally curing polymers require an adapted imprint process. The process scheme comprising heating, plateau ("imprint temperature") and cooling phases, which is usually applied to thermoplastics, did not give satisfactory patterns. When the imprinted polymer was cooled down in the press after the plateau phase, a displacement of the patterns on the wafer was observed. This was avoided, when the cooling phase was omitted and the stamp was released at the imprint temperature [4]. But high temperature and long time were necessary, which is not consistent with a technology designed for mass production.

In the starting model system the curing reaction is a pure thermal polymerization. The curing rate is distinctly increased by admixture of free-radical initiators to the thermally crosslinking polymer. The mould can already be released after
10 minutes, whereas the imprint temperature was only 100 °C in this case (Fig. 8).

![Graph showing temperature and pressure over time for two different stages.

Fig. 7. Process example for model prepolymer (imprint temperature 190 °C, imprint time 60 min)

![Graph showing temperature and pressure over time for a thermally curing polymer.

Fig. 8. Process example for an initiated thermally curing polymer system (imprint temperature 100 °C, imprint time 10 min)

Fig. 9 shows test patterns of imprinted initiated thermally curing polymer

![Image of test patterns imprinted in initiated thermally curing polymer.

Fig. 9. Test patterns imprinted in initiated thermally curing polymer (film thickness 230 nm, 200 nm single lines)

5.2 Photochemically curing polymers

Photochemically curing epoxy-based prepolymer were prepared with $T_g$'s between 35 – 65 °C. Main components are a mixture of epoxy resins and a photo acid generator. Due to the low glass temperature of the prepolymer imprinting temperatures as low as 80 – 100 °C are possible. Imprint edges of only 30 – 60 s can be applied. The curing reaction and structural stabilization including UV flood exposure and post-exposure bake is performed after imprinting. Physical data of the polymer is summarized in Table 4; Fig. 10 shows the steps of the imprint process.

Table 4. Physical properties of epoxy prepolymer

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight $M_w$</td>
<td>7,000</td>
</tr>
<tr>
<td>Density</td>
<td>1.2 g/ml</td>
</tr>
<tr>
<td>Glass transition temperature $T_g$</td>
<td>30 - 65 °C</td>
</tr>
</tbody>
</table>

![Diagram illustrating the imprint process.

Fig. 10. Imprint process for photochemically curing polymer

![Image of patterns of epoxy-based photochemically curing polymer.

Fig. 11. Patterns of epoxy-based photochemically curing polymer (film thickness 200 nm, 100 nm trenches, 200 nm pitch)

5.3 Specific applications of curing polymers

Of course curing polymers can be used working as resists for pattern transfer. The two systems exhibit high plasma etch resistance superior to PMMA. Polymer series for NIL derived from the described model compounds have been commercialised by micro resist technology GmbH as mr-I 9000 (thermally curing) and mr-L 6000 (photochemically curing) (Table 5).

Table 5. Etch rate of curing polymers for NIL (CHF$_3$ plasma)

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<td>110</td>
</tr>
<tr>
<td>mr-L 6000</td>
<td>80</td>
</tr>
</tbody>
</table>
It is well known that small and periodic patterns in the nm range are much easier imprinted than larger μm scale patterns due to polymer transport phenomena. The developed photochemically curing polymer works as a negative tone photoresist, too. Thus a combination of NIL with optical lithography was considered to be advantageous for the definition of coexistent small and large patterns in one layout. It could be proven that mix and match of nanoimprint and UV lithography is possible with this polymer [5]. The glass transition of the resist increased during the imprint and the lithographic sensitivity of the resist decreased slightly. Nevertheless it could be successfully patterned by UV lithography (Fig. 12).

Fig. 12. Process of mix and match of nanoimprint and UV lithography

In the first step a pattern relief was produced through imprinting. In the second step this relief was contact printed by UV lithography and then developed. Depending on the plasma etch conditions (oxygen or fluorine containing plasmas) patterns of quite different feature size can be created this way, where the small nanometre-scaled patterns are defined by the imprint and the larger patterns by UV lithography, or a three step profile is attained (Fig. 12, step 4).

In both the thermally and photochemically curing polymers a tight macromolecular network forms, when the polymers are fully cured. The cured patterns are thermally and mechanically stable so that they can be applied as etch masks, as well as for permanent applications. For demonstrating their stability these materials have been used as stamps for NIL themselves [6]. It was possible to successfully replicate patterns imprinted in the two curing polymers in another polymer film. The fabrication of stamps for NIL is a critical and very costly process step. Hence, it is attractive to use the original stamp made of Silicon, Nickel or quartz only as a master and use the replications in the polymers as working stamps.

6. Outlook

Several polymers have been designed for nanoimprint lithography and are commercially available: thermoplastic polymers with different Tg and curing polymers. The plasma etch resistance of all polymers is superior to PMMA. Curing polymers are attractive candidates for permanent applications, in particular for plastic stamp fabrication. Besides more general demands concerning such as low viscosity during imprinting, low imprint time or high plasma etch resistance, many specific requirements exist depending on given applications. Since applications of NIL are proposed not only in microelectronics, but also in optics, micro and nanofluidics, nanomechanics, biology and further areas, the interest in functional polymers will increase. It is a challenging task for the polymer scientists and chemists to develop and provide these materials.

References