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mr-NIL 6000LT – Epoxy-based curing resist for combined thermal and UV nanoimprint lithography below 50 °C

Christine Schuster *, Freimut Reuther, Anett Kolander, Gabi Gruetzner

Micro Resist Technology GmbH, Koepenicker Str. 325, 12555 Berlin, Germany

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ABSTRACT

The aim of the work presented here was to develop curing polymers for nanoimprint lithography (NIL) enabling short cycle time, low imprint temperature, and an isothermal imprint process. The result is mr-NIL 6000LT: A photochemically curing polymer system for isothermal imprinting by combined thermal and UV nanoimprint lithography. It allows a lower imprint temperature than materials presented previously [C. Schuster, M. Kubenz, F. Reuther, M. Fink, G. Grützner, mr-NIL 6000 – New epoxy-based curing resist for efficient processing in combined thermal and UV nanoimprint lithography, in: Proceedings of SPIE 6517 2007, 65172B.; D.W. Johnson, H. Miller, M. Kubenz, F. Reuther, G. Grützner, Nanoimprinting with SU-8 Epoxy Resists, in: Proceedings of SPIE 6517 2007, 65172A.].

The material system chosen is based on a blend of epoxy resins and a photo acid generator. Such epoxy resists cure during the imprint step in combined thermal and UV nanoimprint lithography. Initiated by UV exposure the cationic polymerisation occurs at elevated temperature forming a polymer pattern with significantly increased thermal stability compared to the uncured system.

Apart from the material development leading to mr-NIL 6000LT the correlations between the parameters imprint temperature, exposure time and post exposure hold time are investigated in this work. With the applied resin combination a T_g of −15 °C is obtained. This enables the formation of solid films at room temperature after spin-coating and prebake and nevertheless imprint temperatures in the range of 45–50 °C, which is a distinct decrease compared to the 100–110 °C needed for the previously introduced mr-NIL 6000 [C. Schuster, M. Kubenz, F. Reuther, M. Fink, G. Grützner, mr-NIL 6000 – New epoxy-based curing resist for efficient processing in combined thermal and UV nanoimprint lithography, in: Proceedings of SPIE 6517 2007, 65172B.] or the 65–70 °C necessary for defect-free imprinting of the epoxy-based polymer described in [D.W. Johnson, H. Miller, M. Kubenz, F. Reuther, G. Grützner, Nanoimprinting with SU-8 Epoxy Resists, in: Proceedings of SPIE 6517 2007, 65172A.]. mr-NIL 6000LT exhibits good dimensional stability at 120 °C after curing during the imprint process. This is sufficient for an isothermal imprint process as well as subsequent processes, e.g. metallization or etching.

1. Introduction

The aim was to develop curing polymers for nanoimprint lithography (NIL) enabling a low imprint temperature, short cycle time and an isothermal imprint process.

The requirements to an epoxy resist for the application in NIL are very different from those of radiation-based lithography. Essentially, high sensitivity is important for fast curing and short cycle time. Furthermore, the glass transition temperature (T_g) of the resist system before curing is vital for the imprint temperature to be chosen.

Low imprint temperatures are important for NIL processes, e.g. when thermally sensitive substrates are used and/or the thermal expansion shall be minimized. In such cases a lower temperature, if possible imprinting at room temperature as in UV-NIL, is preferred. On the other hand, UV-NIL can have the disadvantage that the liquid films to be imprinted tend to suffer from particle contamination to greater extent than solid films. Therefore a material was to be developed that forms solid films at room temperature and nevertheless has a glass transition temperature T_g low enough to enable an imprint temperature as low as possible. This can be accomplished with a resist that cures fast enough even at low imprint temperatures.

An isothermal imprint process, i.e. omitting the cooling phase and demoulding at the imprint temperature, further reduces the cycle time and avoids defects caused by different thermal expansion coefficients of substrate, imprinted polymer, and mould.

* Corresponding author. Tel./fax: +49 30 65762192.
E-mail address: c.schuster@microresist.de (C. Schuster).

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2. Experimental

The tested materials consist of a blend of epoxy resins, a photo acid generator (PAG), solvents and additives. The experimental results presented here refer to the final resist composition, mr-NIL 6000LT, which was chosen after screening by imprinting all resist recipes at temperatures of 40–70 °C and allows an imprint temperature of 45–50 °C.

A Mettler-Toledo DSC822 tool was available for T_g measurements of the different epoxy resin blends. DSC heating curves were recorded from −65 to 120 °C with a heating rate of 10 K/min.

For the imprinting tests 2 in. silicon substrates were used. Before coating they were oxygen plasma treated.

mr-NIL 6000. 2LT films of 200 nm thickness were prepared on the substrate by spin-coating at 3000 rpm for 30 s followed by a softbake on a hotplate at 120 °C for 3 min.

UV transparent moulds were fabricated by twofold pattern replication from the original mould with Ormostamp, a UV curable inorganic–organic hybrid polymer (*micro resist technology* GmbH) [2], and coated with the release agent tridecafluoro-(1,1,2,2)-tetrahydrooctyl-trichlorsilane (F_{13}TCS) from the gas phase.

A NanoImprinter NIL 2.5 in. (Obducat AB, Malmoe, Sweden) was used for the experiments. With the applied tool it is possible to heat and UV-expose the samples simultaneously. The UV unit supplies an intensity of 35 mW/cm^2 (measured at 365 nm). The imprint temperature was 40–70 °C for screening and 45 and 50 °C for the process development with the final resist composition. The imprint pressure was 30 bar. UV exposure started 1 min after applying the imprint pressure to allow the material to fill the mould cavities (flow time). The exposure time was 5, 10, 15, 20, 25 or 30 s. In most tests the exposed wafer was kept at the imprint temperature and pressure for a post exposure hold time of 15 s before demoulding. Additionally, processes without post exposure hold time were tested, i.e. the mould was released immediately after the UV exposure.

The quality of the imprints was characterized by optical microscopy to estimate the filling of the mould cavities and by SEM in order to detect pattern deformation or other defects such as ripped-off patterns.

For further characterization the imprinted patterns were put onto a hotplate at 120 °C for 10 min in order to check the thermal pattern stability. Insufficient cross-linking of the resist would be detected by reflow or some rounding of the resist patterns. The pattern quality after the flow test was inspected by SEM.

3. Results and discussion

3.1. Material development

mr-NIL 6000LT is an epoxy resist that cures during the imprint step in combined thermal and UV nanoimprint lithography. Cationic polymerisation is initiated by UV exposure and occurs at elevated temperature. Polymer patterns are formed with significantly increased thermal stability compared to the uncured system (shown in [1] for an epoxy resist at 100 °C imprint temperature).

Different epoxy resins were blended in various ratios. Resists with these resin blends were tested in imprinting processes with temperatures of 40, 50, 60 and 70 °C. The screening resulted in a favoured resist composition. The blend used in the final resist composition has a T_g of −15 °C. This T_g is high enough to enable the formation of slightly sticky solid films at room temperature after spin-coating and softbake. On the other hand T_g is low enough to allow an imprint temperature as low as 45–50 °C.

The necessary high reactivity of the resist already at lower curing temperatures was obtained by adjusting PAG content, PAG reactivity and resin reactivity.

3.2. Principle of the applied nanoimprint lithography process

An isothermal process of combined thermal and UV nanoimprint lithography was utilized for the curing polymers (Process scheme see Fig. 1).

In the beginning of the imprint cycle there is a "flow time" for the complete filling of the mould cavities. The UV exposure after the "flow time" is optionally followed by a "post exposure hold time" at imprint temperature and pressure. During the flow time there is no or only a negligible increase in T_g. A significant T_g increase occurs during UV exposure and subsequent post exposure hold time due to the polymer cross-linking (see Fig. 2).

3.3. Process development

After screening and definition of the final resist recipe, the imprint conditions were further optimised with the aim of imprint temperatures and cycle times as low as possible.

One possibility to reduce the imprint cycle time is to apply an isothermal process, i.e. to omit the cooling phase and demould at the imprint temperature. This also avoids possible defects that may be caused by different thermal expansion coefficients of substrate, imprinted polymer and mould.

Clearly, the increase of the glass transition temperature of final resist recipe, mr-NIL 6000LT, during the imprint is sufficient to allow an isothermal process. The imprinted patterns are effectively cured, and the mechanical stability is high enough for demoulding at the imprint temperature of 45–50 °C.

Variation of imprint temperature, UV exposure time and post exposure hold time – maintaining the flow time of 1 min and the imprint pressure of 30 bar – resulted in the most favourable imprint processes for 50 and 45 °C imprint temperature shown in

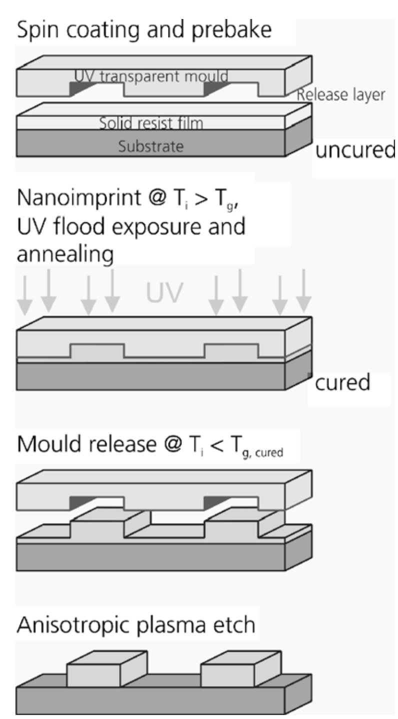

Fig. 1. Applied nanoimprint process.

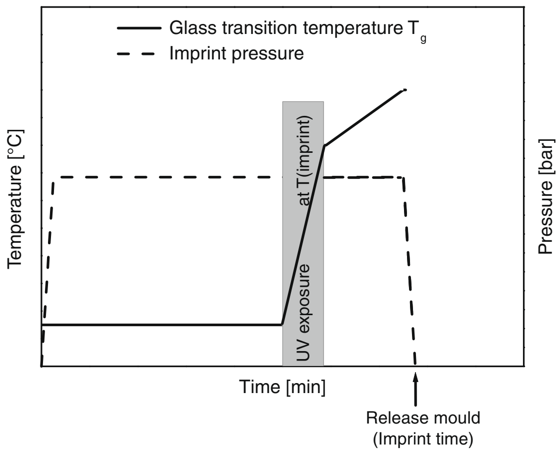

Fig. 2. Schematic diagram – T_g change during the imprint process.

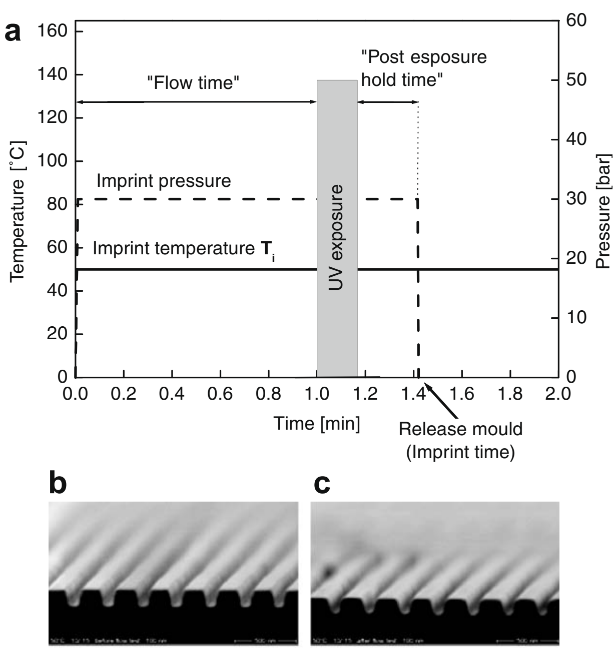

Fig. 3. Imprinting at 50 °C, 10 s UV exposure, 15 s post exposure hold time: Process scheme (top, a), imprinted 200 nm lines/100 nm trenches before (bottom left, b) and after (bottom right, c) flow test.

Fig. 3–5. The displayed respective resist patterns refer to the state before and after the flow tests at 120 °C for 10 min. These are the processes with the shortest possible exposure times for the respective temperatures. Any shorter exposure times, or omitting the post exposure hold time in case of 45 °C imprint temperature, resulted in pattern rounding or deformation after the flow test.

The flow tests (hotplate, 120 °C, 10 min) demonstrate the thermal pattern stability for all three optimised imprint processes.

A comparison of the optimum processes for 45 and 50 °C shows that the lower imprint temperature requires a higher exposure dose to obtain sufficient pattern stability. Contrary to 45 °C the post exposure hold time can be omitted at 50 °C imprint temperature.

The preferred process depends on the parameters the user emphasises. If a low cycle time is important the process with 50 °C imprint temperature, 10 s UV exposure without the post exposure hold time will be preferable. If an imprint temperature

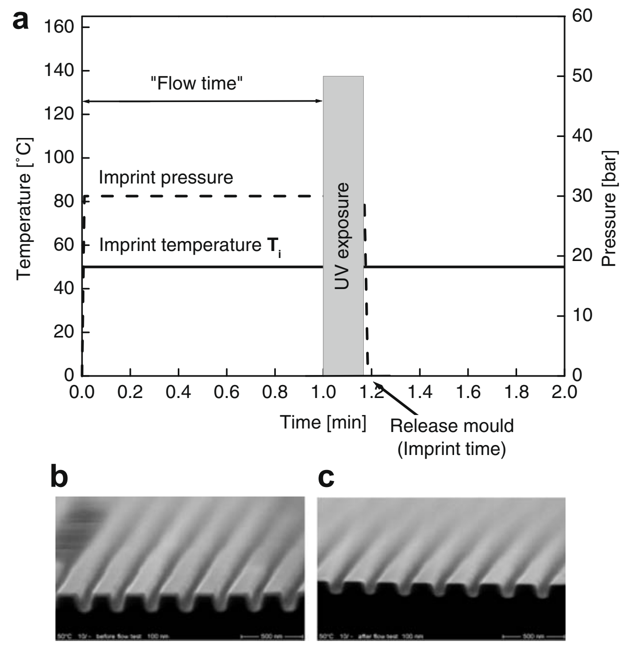

Fig. 4. Imprinting at 50 °C, 10 s UV exposure, no post exposure hold time: Process scheme (top, a), imprinted 200 nm lines/100 nm trenches before (bottom left, b) and after (bottom right, c) flow test.

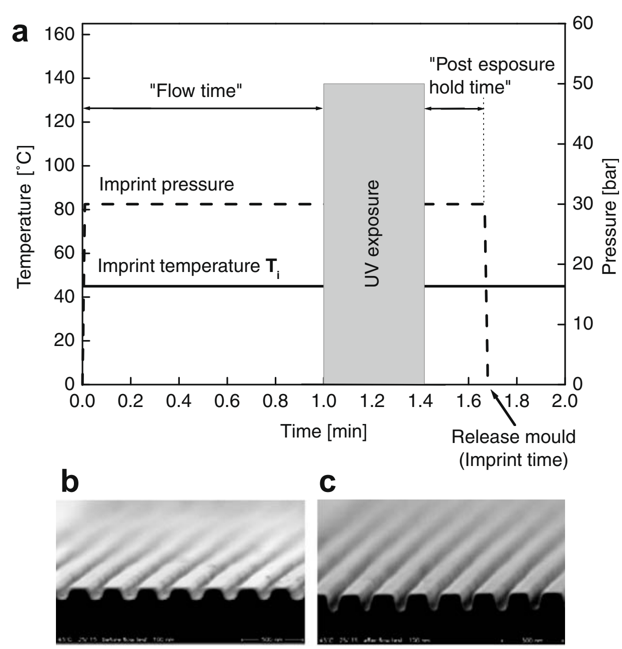

Fig. 5. Imprinting at 45 °C, 25 s UV exposure, 15 s post exposure hold time: Process scheme (top, a), imprinted 200 nm lines/100 nm trenches before (bottom left, b) and after (bottom right, c) flow test.

as low as possible is necessary the process shown in Fig. 5 with 45 °C, 25 s UV exposure and 15 s post exposure hold time can be applied.

The most beneficial process would comprise an imprint temperature of 50 °C, 10 s UV exposure and a 15 s post exposure hold time.

4. Conclusions

mr-NIL 6000LT is a photochemically curing polymer system for isothermal imprinting by combined thermal and UV nanoimprint lithography. In the applied imprint processes the imprinted resist is exposed by UV light and the curing reaction occurs at the imprint temperature immediately in the machine.

The polymer forms a solid film at room temperature after spincoating and softbake; it is easy to handle, the risk of particle contamination of the spin-coated films is reduced compared to liquid films. Nevertheless the polymer system can be imprinted at temperatures as low as 45–50 °C. Despite the low imprint temperature it cures during the imprint causing a T_g increase that is sufficient for an isothermal imprint process, i.e. the demoulding at the imprint temperature, and for a good dimensional stability at 120 °C making the imprinted patterns well suited for subsequent processes, such as metallization or etching.

Acknowledgement

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References

[1] C. Schuster, M. Kubenz, F. Reuther, M. Fink, G. Grützner, mr-NIL 6000 – New epoxy-based curing resist for efficient processing in combined thermal and UV nanoimprint lithography, in: Proceedings of SPIE 6517 2007, 65172B.
[2] A. Klukowska, A. Kolander, I. Bergmair, M. Mühlberger, H. Leichtfried, F. Reuther, G. Grützner, R. Schöftner, Micro- and nano-engineering 2008, International conference, Athens, Greece, Sept. 15–18, 2008.