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Thermal nanoimprint resist for the fabrication of high-aspect-ratio patterns

M. Messerschmidt [a,*], A. Schleunitz [a,b], C. Spreu [b], T. Werner [c], M. Vogler [a], F. Reuther [a], A. Bertz [c], H. Schift [b], G. Grützner [a]

[a] micro resist technology GmbH, 12555 Berlin, Köpenicker Straße 325, Germany
[b] Paul Scherrer Institute, Laboratory for Micro- and Nanotechnology, 5232 Villigen, Switzerland
[c] Fraunhofer-Institut für Elektronische Nanosysteme ENAS, 09126 Chemnitz, Technologie-Campus 3, Germany

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ABSTRACT

We report a newly developed thermal nanoimprint (T-NIL) resist specifically engineered for the implementation in a bilayer system rendering the fabrication of high-aspect-ratio patterns. The synthesis of the T-NIL resist was accomplished by applying a free radical copolymerization of adequate comonomers. Due to the modular architecture of the terpolymer, the rather different material properties are directly adjusted by varying the amount of the comonomers and also by tuning the polymerization conditions like temperature and the amount of initiator. Following this synthetic strategy, the Si content for a sufficient oxygen plasma resistance as well as an excellent flowability behavior for a significant reduction of the overall processing cycle time could be easily achieved. Moreover, the already good mould release properties of the pure T-NIL resist can be further improved by the addition of a small amount of a fluorinated additive leading to a very low defect rate of the imprinted structures.

1. Introduction

Nanoimprint lithography (NIL) has emerged as a powerful technique in the fabrication of micro- and nanostructures [1]. Up to now, most of the commonly used NIL resists work satisfactorily for the imprinting of patterns with moderate aspect ratios of maximum three. But for specific applications, e.g. high-brightness LEDs, features with higher aspect ratios are highly advantageous or even necessary. Generally, the manufacturing of such high-aspect-ratio patterns demands specially designed resists which are applicable in bilayer systems [2]. In such systems, firstly a thick organic under layer or transfer-layer (ca. 1 μm) is spin-coated onto the substrate followed by the preparation of a thinner layer consisting of a Si-containing resist. As the Si-containing resist features a significantly higher resistance toward oxygen plasma compared to the purely organic material of the transfer layer, the relief of the imprinted silicon-containing layer can be strongly magnified by applying an oxygen reactive ion etching (RIE) step. The obtained high-aspect-ratio patterns can then further transferred into the underlying substrate employing additional etching procedures [2]. Such bilayer systems are already established for UV-based NIL [3], but only few literature has been published for thermal nanoimprint lithography (T-NIL) [4]. An industrial applicability of such a T-NIL resist requires additionally short processing cycles and a high patterning fidelity. Accordingly, the T-NIL resist needs an excellent inherent flowability to ensure a fast filling of the structures, whereas a low polarity of the material is favorable to minimize surface energies and thus defects during the demoulding step. In this contribution, we present the synthetic approach and the characterization of a new T-NIL resist as well as the investigated film forming properties, the imprinting behavior and the plasma etch resistance toward RIE with oxygen and a mixture of fluorinated gases.

2. Experimental

2.1. Materials

All employed chemicals were of analytical grade and used as received except for the initiator 2,2′-azobis(isobutyronitrile) (AIBN) which was purified by recrystallization from ethanol prior to use.

2.2. Polymer synthesis and characterization

The preparation of the terpolymer SiPol was performed analogously as described elsewhere [5].

The glass transition temperature (T_g) of SiPol was investigated by a DSC822e from Mettler Toledo employing the Star^e Software (Version 9.01). The measurement was run under a nitrogen atmosphere with a flow rate of 10 K/min. For determination of the T_g only the second heating cycle was applied using the half-step method. The molecular weight and the polydispersity index (PDI) of SiPol was determined by GPC analysis using the integrated

* Corresponding author.
E-mail address: m.messerschmidt@microresist.de (M. Messerschmidt).

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GPC system PL-GPC 50 Plus (Polymer Laboratories, Varian Inc. Company) equipped with two columns (Resipore 300 × 7.5 mm, Varian Inc.) and a RI detector. The GPC measurement was conducted with THF as eluent with a flow rate of 1 mL/min at 40 °C. Narrowly distributed polystyrene standards were applied for calibration.

2.3. Preparation of polymer layers and their characterization

The employed 2 or 4-in. silicon wafers were cleaned in an oxygen plasma before use. All polymer layers were prepared by spin-coating on a DELTA 6 RC spin coater module from Süss MicroTec. The polymer solutions for the preparation of the organic transfer layers (15 wt.-% organic polymer dissolved in 2-isopropoxyethanol) were purified by filtration with 0.2 μm filters followed by spin-coating applying 3000 rpm and annealing of the deposited layers at 175 °C for 5 min. Likewise, the polymer solutions of the SiPol terpolymer were firstly purified by filtering (0.1 μm filters) and then applied for spin-coating. The as-prepared films were directly annealed after preparation for 2 minutes at 140 °C. All film thicknesses were measured using a FTP 500 from Sentech Instruments or a Dektak 8 from Veeco Instruments Inc.

2.4. Imprint experiments and characterization of imprinted patterns

The imprint experiments were conducted either on a Nanoimprinter NIL-2.5 from Obducat or on a Jenoptik HEX03 NIL machine. Optical photographs of imprinted structures were recorded using an Olympus BX51M equipped with a Color View Soft Imaging System.

2.5. RIE etching experiments

The evaluation of the etching rates of the silicon containing SiPol terpolymer and an organic based reference material (mr-I 8000R) toward oxygen RIE and was investigated on a Plasmalab System 100 ICP from Oxford Instruments applying the following etching parameters: 30 sccm O_2, 1300 W ICP, 50 W bias, 0.7 Pa, 5.0 min. Accordingly, the etching rates of the polymers toward a mixture of the plasma gases CHF_3 and CF_4 was also conducted on a Plasmalab System 100 ICP from Oxford Instruments applying the following etching parameters: 1300 W ICP, 50 W bias, 1 Pa, 10 °C, 10 minutes.

3. Results and discussion

3.1. Polymer synthesis and characterization

Free radical copolymerization was considered to be an appropriate synthetic methodology for the synthesis of the resist material as the tailoring of the material properties can be directly accomplished by varying the amount of the employed comonomers and additionally by adjusting crucial reaction parameters of polymerization like the temperature for example. Besides of the comonomers, a sufficient amount of dioxane was added to the reaction flask as a solvent for both the comonomers as well as the formed polymers enabling a good mixing of all compounds during the polymerization.

Basically, we found that in total three different comonomers are needed in order to incorporate all relevant material properties like a sufficient high Si-content (monomer A), an excellent inherent flowability (monomer B) as well as an adjusted glass transition temperature (monomer C) into the T-NIL resist material. All employed comonomers were specifically chosen from such monomer families (see Table 1) which typically prone to the formation of nearly random terpolymers so that the polymer chains presumably feature a rather statistical distribution of the three different repeating units along the polymer chains. Consequently, as a first approximation, the composition of the different comonomer units within the terpolymer chains is likely to be close to that of the comonomers within the reaction batch before starting the polymerization. Based on this assumption, we synthesized a bunch of different terpolymers with varying amounts of the three comonomers. Table 1 summarizes the generic structures as well as the concentration ranges of the applied comonomers A, B and C that impart specific material properties to the obtained terpolymers.

The obtained terpolymers were subsequently evaluated in terms of their film forming behavior and film homogeneity as well as their flowability and demoulding performance. By applying this empirical evaluation strategy, we were able to finally figure out the terpolymer SiPol with the best overall performance. Accordingly, a distinct investigation of the terpolymer composition by e.g. NMR analysis was therefore omitted since it would have provided no further information facilitating the selection of the terpolymer with the best material properties.

The polymerization of the SiPol was conducted employing a sufficient amount of the Si-containing comonomer A so that a silicon content of 11 wt.-% is obtained in the final SiPol when a random polymerization is assumed. Different working groups independently found that a Si content of approximately 10 wt.-% within a polymer is necessary in order to form a protecting silicon oxide layer during an oxygen plasma etch process [2]. Interestingly, the chemical structure of the polymer is less important [6]. In order to incorporate excellent flowability characteristics during thermal imprinting to the terpolymer, comonomer B was employed while the adjustment of the glass transition temperature (T_g) at 63 °C was accomplished by a specific amount of comonomer C. The T_g of SiPol was determined by DSC analysis of the second heating cycle using the half-step method. This temperature is regarded to be ideal, because it ensures an imprinting at relatively moderate temperatures around 120 and 130 °C and has still a sufficient high thermal stability to withstand the thermal loading in subsequent plasma etch procedures.

Since polymer chains with high molecular weights typically tend to form entanglements which impair the flowability of a polymeric resist material, we favored a comparatively low molecular weight around 10,000 g/mol where the formation of such entanglements is rather unlikely for the SiPol terpolymer. To this end, the crucial reaction parameters like the molar ratio between the comonomers and the initiator AIBN was set to only 50:1, and furthermore, the polymerization was carried out at a comparatively high temperature of 90 °C that additionally fosters the formation of polymer chains with lower molecular weight. The molecular

Table 1
Generic structures and concentration ranges of the employed comonomers A, B and C imparting characteristic material properties to the prepared terpolymers.

Type of monomer	Characteristic material property	Generic monomer structure	Concentration range [wt.-%]
A (Methacrylate-based)	Imparts high O_2 plasma resistance due to Si	HC=C(CH_3)–(C=O)–O–R_1 (R_1 contains Si)	50–70
B (Styrene-based)	Improves the flowability behavior	HC=CH-R_2	25–40
C (Acrylate-based)	Precise adjustment of the glass transition temperature (T_g)	HC=CH–(C=O)–O–R_3	5–10